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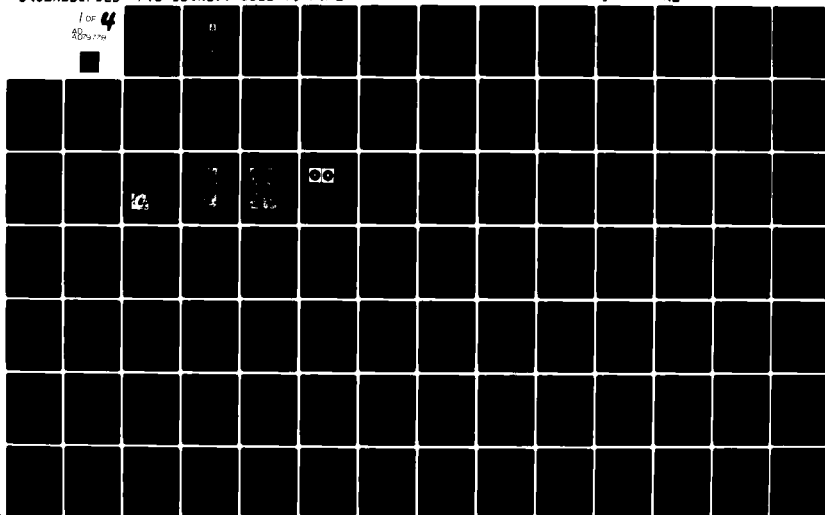
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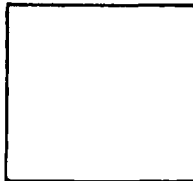
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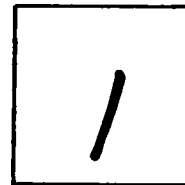
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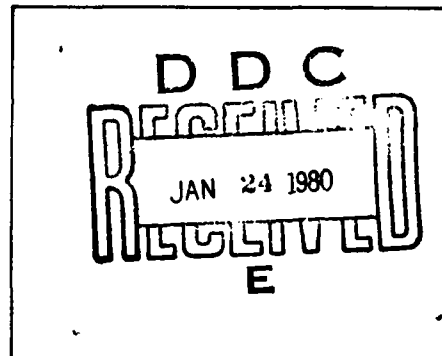
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STRUCTURE AND PROPERTIES OF POLYURETHANES

by

Yu. S. Lipatov, Yu. Yu. Kercha, and L. M. Sergeyeva



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Chapter VII. PHYSICOMECHANICAL PROPERTIES OF POLYURETHANES.

CONNECTION BETWEEN BASIC PHYSICOMECHANICAL PROPERTIES OF POLYURETHANES AND STRUCTURE.

Interest in polyurethane is determined, first of all, by those physicomachanical indices which possess the materials on their basis. High resistance to abrasion and significant mechanical strength make it possible to use rubbers from urethane rubbers in the machine-building and other branches of industry as structural material. Recommended well themselves polyurethane glues and coatings, polyurethane icams, fibers.

Obtaining materials on basis it is polyurethane with this broad band of properties caused by application/use with their synthesis of the chemical compounds of different class. Therefore to questions of the bond between the structure it is polyurethane and their basic physicomachanical properties devoted large number of works and survey/coverages [167, 175, 287, 290, 305, 306, 317].

Since these questions are illuminated in detail in the monograph of Saunders and Frisch [114], then we mainly will only examine the influence of the nature of the comprising components on basic physicommechanical properties it is polyurethane, using the data, published in recent years.

Effect of the nature of polyether/polyester and its molecular weight.

The properties of polyurethane elastomers to a considerable degree depend on structure and molecular weight of basic component - polyether/polyester. Studied the effect of the structure of polyester on the properties of elastomers on the basis of 1,5-naphthylenediisocyanate [175, 305] (Table 42) it is polyurethane on the basis of diphenylmethane diisocyanate and 1,4-butanediol [287] (Table 43).

As can be seen from given data, the mechanical properties it is polyurethane they affect an increase of the quantity of methylene groups in polyether/polyester and the presence of side chains in glycol component, which to high degree decreases the strength. Deterioration in some mechanical characteristics in these cases is bonded with a reduction in the concentration of ester groups, which

decreases a quantity of molecular bonds, caused by the reaction of these groups with other polar groups in chains is polyurethane.

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Analogously are lowered the physicomachanical properties it is polyurethane during the replacement of polyester on simple, which, as showed Smith and Magnusson [318], is bonded with the absence of ester groups in polyurethane on the basis polyethers. They studied elastomers on the basis of simple and polyesters, 2,4-toluenediisocyanate and trimethylol propane. As polyether was taken PPG, as complex ones served polyether/polyester, obtained during copolymerization methyl- ϵ - and ϵ -caprolactone. During the comparison of some characteristics of both, it is polyurethane it turned out that if the modulus of elasticity of polyurethane on the basis of PPG was 9.1-12.2 kg/cm², then during the replacement of PPG by polyester it was raised to 18.5-24.3 kg/cm².

Table 42. Dependence of the properties of polyurethane elastomers on the structure of polyesters.

(1) Гликоль	(2) Кислота	(3) Предел прочности при растяжении, кг/см ²	(4) Относительное удлинение при разрыве, %	(5) Предел прочности на раздир, кг/см ²
Этиленгликоль (6)	Янтарная (7)	273	625	119
	Адипиновая (8)	350	640	158
	Дигликолевая (9)	266	570	147
1,2-Пропиленгликоль (10)	Адипиновая (8)	217	480	91
2,3-Бутиленгликоль (11)	" (8)	179	630	91

Key: (1). Glycol. (2). Acid. (3). Tensile strength, kg/cm². (4). Elongation at rupture. (5). Limit of strength to tear, kg/cm². (6). Ethylene glycol. (7). Succinic. (8). Adipic. (9). Diglycollic. (10). Propyleneglycol. (11). Butyleneglycol.

Table 43. Properties of polyurethane elastomers on the basis of complex polyetherdiol.

(1) Сложный полиэфир	(2) Предел прочности при растяжении, кг/см ²	(3) Относительное удлинение при разрыве, %	(4) Остаточное удлинение, %	(5) Модуль упругости при 30% ном. удлинении, кг/см ²	(6) Предел прочности на раздир, кг/см ²	(7) Твердость по Шору (шкала В)
Полиэтиленадипинат (8)	483	590	25	108.5	43.2	60
Поли-1,4-бутиленадипинат (4)	420	510	15	133	48.6	70
Поли-1,5-пентаметиленадипинат (10)	441	450	10	126	10.8	60
Поли-1,3-бутиленадипинат (8)	224	520	15	77	18.0	58
Полиэтиленисукцинат (11)	476	420	40	224	36.0	75
Поли-2,3-бутиленисукцинат (12)	245	380	105	—	93.6	85
Полинеопентилсукцинат (13)	182	400	70	140	41.4	67

Key: (1). Polyester. (2). Tensile strength, kg/cm². (3). Elongation at rupture, o/o. (4). Permanent elongation. (5). Modulus of

elasticity with 300o/o elongation, kg/cm². (6). Limit of strength to tear, kg/cm². (7). Shore hardness (scale B). (8).

Polyethylenedipate. (9). Poly-1,4-butylenedipate. (10).

Poly-1,5-pentmethylenedipate. (11). Polyethylenesuccinate. (12).

Poly-2,3-butylenesuccinate. (13). Polyneopentylsuccinate.

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According to [208], polyurethane elastomers on the basis of polyesters (polyethyleneglycoladipate) possess large strength, wear resistance, stability to the action/effect of solvents, than polyurethane on the basis polyethers (polytetramethyleneglycol and polyoxypropyleneglycol). This tells about the great effect of ester groups on mechanical properties it is polyurethane. The strength of the molecular bonds, formed by ester groups with other groups of polymer chains, is so great which frequently succeeds in obtaining the linear polyurethane elastomers, which possess excellent mechanical properties at room temperature [306].

A change in molecular weight of polyester insignificantly affects initial properties it is polyurethane, as shown in the example of polyethyleneglycoladipate [175, 305] (Table 44). During storage elastomers on the basis of polyether/polyesters with large molecular weight it is slow they are crystallized. With the smallest

of studied molecular weights (1385) was observed the smallest capability for crystallization, but strength to tear and elasticity they were small. A change in molecular weight from 2160 to 4680 did not virtually affect the mechanical properties of polymers on their basis, but from 1180 to 2160, it increased strength by tear and elongation.

In accordance with findings, optimal molecular weight of polyethyleneglycoladipate used for synthesis is polyurethane, considered molecular weight of order 2000.

The study of the physicommechanical properties of polyurethane with different molecular weights of polyisophthalate, which presents the mixture of poly-1,4-aminobutylenedipate (PBA), poly-1,5-aminobisphthalate (PAI), polyethylenedisophthalate (PEI) [196] showed that molecular weight of polyester considerably changes physical properties it is polyurethane (Table 45).

Table 44. Dependence of the properties of polyurethane elastomers on molecular weight of polyether/polyester and quantity of diisocyanate.

(1) M полиэфира	(2) Количество диизоциана- та, г/100 г полиэфира	(3) Предел проч- ности при растяжении, кг/см ²	(4) Относитель- ное удлине- ние при раз- рыве, %	(5) Модуль уп- ругости при 300% ном удли- нении, кг/см ²	(6) Предел проч- ности на раз- дир, кг/см ²	(7) Эластич- ность, %	(8) Твердость по Шору (шкала А)
2290	15.2	392	680	93	189	58	65—71
3500	11.9	346	560	130	249	65	67—73
3100	12.6	305	610	111	172	59	68—73
2440	14.6	350	645	112	186	59	71—76
2080	16.2	385	635	130	186	60	71—76
1385	21.6	371	645	109	125	50	74—77

Key: (1). polyether/polyester. (2). Quantity of diisocyanate, g/100 ml of polyether/polyester. (3). Tensile strength, kg/cm². (4). Elongation at rupture. (5). Module/modulus of elasticity during 300% elongation, kg/cm². (6). Limit of strength to tear, kg/cm². (7). Elasticity. (8). Shore hardness (scale A).

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Specimen/samples with the greatest tensile strength are obtained on the basis of polyisocphthalate with a molecular weight of 600. An increase in molecular weight to 2000 decreases the tensile strength it is polyurethane.

In work [266] investigated the effect of molecular weight of the polyester of adipic acid and mixture of ethylene- and propyleneglycol

(molecular ratio 70:30) on the value of module/modulus it is polyurethane. It is shown, which with an increase in molecular weight of polyether/polyester from 1200 to 3200 values of module/modulus with 100, 200 and 300% elongation is lowered.

The effect of molecular weight polyether on mechanical properties of polyurethanes [167] is studied on prepolymers with 2,4-TDI and PPG of different molecular weight with relationship/ratio NCO:OH=2:1; hardener - methylene-bis-o-chloraniline. It is establish/installed, that the tensile strength, module/modulus and some other characteristics are improved with smaller molecular weight (Table 46). With an increase in molecular weight of PPG, descends the abrasability and increases elasticity it is polyurethane.

Polyurethaneacrylate (polyurethane materials on the basis of oligoester, diisocyanates and mono-methacrylic ether/ester of ethylene glycol) possess the best tensile strength with light molecular weights both of simple and complex oligoester [86] (Table 47). With an increase in molecular weight, the strength decreases, but increases relative extension at break.

Table 45. Dependence of the physical properties of polyurethane prepolymer on numerical average molecular weight of polyisophthalate.

(1) М поли- изофталата	(2) Компонента, %			(3) Прочность на разрыв, кг/см ²	(4) Удлинение, %	(5) Твердость по Уэлласу
	ПБА	ПАН	ПЭН			
600	40	10	50	398	575	50
600	40	20	40	454	533	57
600	40	30	30	244	650	53
600	30	10	60	245	400	77
600	30	20	50	362	457	68
600	30	35	35	238	288	66
600	30	50	20	517	463	59
600	20	50	50	348	10	94
2000	60	10	30	232	567	52
2000	60	20	20	139	603	48
2000	50	10	40	194	573	46
2000	50	25	25	381	513	60
2000	50	40	10	111	585	51
2000	40	10	50	227	445	86
2000	40	20	40	226	428	68
2000	35	15	50	293	450	62

Key: (1). M of polyisophthalate. (2). Component. (3). By tensile strength, kg/cm². (4). Elongation, o/o. (5). Hardness per Wellas.

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During the investigation of the effect of molecular weight on the mechanical properties of polyurethane on the basis of TDI and polyoxyethyleneglycol (PEG) is calculated the content of uric and urethane groups [229]. It was established that an increase in molecular weight of oligoester is accompanied by the decrease of the content of urethane and uric groups, which causes a reduction in the strength, but increases elasticity and elongation (Table 48).

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The analogous effect of the molecular weight of oligoester on mechanical properties is observed also for polyurethane coatings [102, 103, 119, 120, 123].

Table 46. Mechanical properties of elastomers on the basis of PPG and 2,4-TDI.

(1) Свойство	МППГ			
	1000	1250	1500	2000
(2) Предел прочности при растяжении, кг/см ²	353	315	245	84
(3) Относительное удлинение при разрыве, %	—	860	—	—
(4) Модуль упругости при 300%-ном удлинении, кг/см ²	147	70	42	28
(5) Прочность на раздир (по Грейвсу), кг/см ²	56	43	40	22
(6) Твердость по Шору (шкала А)	88	77	67	60
(7) Потеря массы при истирании через 1000 циклов (по Таберу), мг	85	60	25	8
(8) Температура хрупкости (по Тиниусу — Олсену), °C	-40	-50	-55	-56
(9) Эластичность по отскоку (по Башору), %	24	20	22	38

Key: (1). Property. (2). Tensile strength, kg/cm². (3). Relative elongation with detachment. (4). Module/modulus of elasticity during 300% elongation, kg/cm². (5). Strength to tear (per Graves), kg/cm². (6). Shore hardness (scale A). (7). Loss of mass during abrasion through 1000 cycles (per Taber), mg. (8). Brittle point (per Tinius-Olsen), °C. (9). Resilience (per Bayshore), o/o.

Table 47. Some physicomachanical properties of polyurethaneacrylate.

(1) Олигоэфирполиколь	МОЭГ	(2) Динизоцианат	(3) Предел прочности при растяжении кг/см ²	(4) Относительное удлинение при разрыве, %	(5) М _с рассчитанное
(6) Полиоксипропиленгликоль	400	(7) 4,4'-Дифенилметандиизоцианат	650	12	386
(4) Адипиновая кислота и этиленгликоль	1000	То же (8)	130	112	585
	2000	" "	60	120	920
	630	2,4-ТДЦ	200	60	413
	1000	"	80	140	535
	1360	"	90	145	656
	1600	"	80	130	672

Key: (1). Oligoesterglycol. (2). Diisocyanate. (3). Tensile strength of kg/cm². (4). Elongation at rupture. (5). calculated. (6). Polyoxypropyleneglycol. (7). Diphenylmethane diisocyanate. (8). The same. (9). Adipic acid and ethylene glycol.

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Thus, a change in molecular weight of initial oligoester makes it possible to vary the properties of polyurethane materials, which is bonded with different concentration of polar groups at different length of oligoester block.

The value of optimal molecular weight of initial polyether/polyester depends on the nature of oligoester and is determined mainly by the flexibility of the latter: the more the flexibility possesses the molecule of oligoester, by the fact with smaller molecular weight it is possible to obtain polyurethane with optimal properties.

Structure of diisocyanate.

Properties of polyurethane they depend on the nature of isocyanate, utilized with synthesis. Table 49 shows the effect of the structure of diisocyanates on the properties of elastomers on the

basis of polyethyleneglycoladipate of molecular weight 2000 [175], as hardener served water.

It was established that the bulky aromatic groups of diisocyanates to a considerable degree contribute to an increase in strength of elastomers. These results will agree with data [287] (Table 50). Module/modulus, strength by tear and hardness are increased both during the introduction of rigid aromatic structures and in the case of diisocyanates without methylene substituents.

Table 48. Characteristics of polyureaurethane films on the basis of TDI and polyethers.

(1) Свойство	(2) Полиол		
	ПЭГ-200	ПЭГ-400	ПЭГ-1000
(3) Содержание уретановых групп, %	21,4	15,6	8,8
(4) Содержание мочевиновых групп, %	10,5	7,7	4,3
(5) Содержание ароматических групп (C ₆ H ₅), %	27,2	19,9	11,1
(6) Максимальная прочность при растяжении, кг/см ²	262,0	210,0	21,0
(7) Максимальное удлинение, %	0	400,0	1000,0

Key: (1). Property. (2). Polyol. (3). Content of urethane groups. (4). Content of uric groups. (5). Content of aromatic groups. (6). Maximum tensile strength, kg/cm². (7). Maximum elongation.

Table 49. Effect of the structure of isocyanates on the properties of polyurethane elastomers.

(1) Диизоцианат	(2) Предел прочности при растяжении, кг/см ²	(3) Относительное удлинение при разрыве, %	(4) Предел прочности на разрыв, кг/см ²
2,4-Толуиленизоцианат (5)	200—249	730	83
1,5-Нафтиленизоцианат (6)	308	765	166
2,7-Флуоренизоцианат (7)	434	660	141

Key: (1). Diisocyanate. (2). Tensile strength, kg/cm². (3). Elongation at rupture. (4). Limit of strength to tear, kg/cm². (5). Toluenediisocyanate. (6). Naphthylenediisocyanate. (7). Fluorenediisocyanate.

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The mechanical properties of elastomers are determined not only by the nature of diisocyanate, but also by the relationship/ratio in it of isomers [290]. Investigated the effect of relationship/ratio 4,4'- and 2,4'-diphenylmethanediisocyanate on mechanical properties it is polyurethane on the basis of polycaprolactone (mol. weight 1050) and of butanediol (Fig. 83) and it is establish/installed, that the fundamental characteristics worsen with an increase in the content of 2,4'-isomer. This phenomenon is bonded with a change in the symmetry of polymer chains during a change in the isomeric composition of diisocyanate.

Effect of the nature of the structure of grid and types of cross connections on properties is polyurethane.

Examining the effect of the nature of components on mechanical properties it is polyurethane, one should, first of all, investigate their role in the structure of the grid of polymers, since to the nature of cross connections in polyurethane, their quantity, regularity of the construction of three-dimensional grid are the main thing by the factors, which condition the physicommechanical properties of polymers.

Many researchers studied the influence of the network density, calculated theoretically or by that determined experimentally, to mechanical properties was polyurethane [130, 186, 224, 287, 305, 317]. For example, is represented the dependence of some mechanical properties of polyurethane rubber SKU-V (on the basis of complex polyfunctional polyether/polyester P-V and 2,-TDI) on the relationship/ratio of TDI: polyether/polyester.

Table 50. Effect of the structure of diisocyanates on the properties of polyurethane elastomers on the basis of polyesters (hardener glycol).

(1) Диизоцианат	(2) Предел прочности при растяжении, кг/см ²	(3) Относительное удлинение при разрыве, %	(4) Остаточное удлинение, %	(5) Модуль упругости при 300%-ном удлинении, кг/см ²	(6) Предел прочности на разрыв, кг/см ²	(7) Твердость по Shore
Нафтилендиизоцианат (8)	301,0	500	85	210,0	36,0	80
Фенилендиизоцианат (9)	447,5	600	25	161,0	54,0	72
2,4-Толулендиизоцианат (10)	322,0	600	1	24,5	27,0	40
4,4'-Дифенилметандиизоцианат (11)	552,5	600	10	112,0	48,6	61
3,3'-Диметил-4,4'-дифенилметандиизоцианат (12)	371,0	500	0	42,0	7,2	47
4,4'-Дифенилизопропилдиизоцианат (13)	245,0	700	10	21,0	16,2	56
3,3'-Диметил-4,4'-толулендиизоцианат (14)	280,0	400	10	161,0	32,4	70

Key: (1). Diisocyanate. (2). Tensile strength, kg/cm². (3). Elongation at rupture. (4). Permanent elongation. (5). Module/modulus of elasticity during 300% elongation, kg/cm². (6). Limit of strength to tear, kg/cm². (7). Shore hardness. (8). Naphthylenediisocyanate. (9). Phenylenediisocyanate. (10). Toluenediisocyanate. (11). Diphenylmethane diisocyanate. (12). Dimethyl-4,4'-diphenylmethanediisocyanate. (13). Diphenylisopropyl diisocyanate. (14). Dimethyl-4,4'-toluenediisocyanate.

During an increase in the relationship/ratio of TDI:polyether/polyester from 0.8 to 1.1 values M_c , determined according to the equilibrium modulus, it varied from 41500 to 1650, tensile strength was increased, and relative elongation continuously fell (Fig. 84).

In other cases the character of the dependence of mechanical properties on network density is more complex [287, 135]. Table 51 gives the results of studying the effect of network density on the basic physicomachanical properties of elastomers on the basis of polyethyleneglycoladipate, diphenylmethane diisocyanate and trimethylol propane [287]. Value M_c is calculated theoretically from stoichiometric composition.

Decrease M_c from 21000 to 5300 leads to softening, strength with extension, elongation, module/modulus and strengths by tear, is increased at the same time elasticity. According to [287], during an increase in the maturing degree because of primary chemical bonds hinders the most advantageous for intermolecular interaction arrangement of chains in space, which decreases the effectiveness of intermolecular interaction. Consequently, great effect on mechanical properties it is polyurethane is exerted secondary molecular bonds.

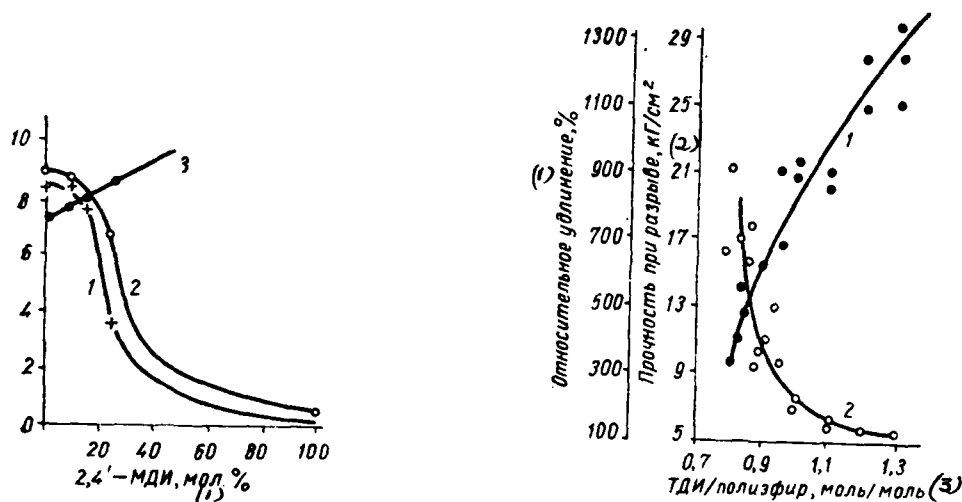


Fig. 83. The dependence of isomeric composition and physical properties of elastomers on the basis of polycaprolactone, butanediol, 4,4'-MDI and 2,4'-MDI: 1 - tensile strength, kgf/cm^2 ($\times 70$); 2 - module/modulus during 100% elongation, (kgf/cm^2 ($\times 7$)); 3 - ultimate elongation, o/o ($\times 100$).

Key: (1). mole.

Fig. 84. Dependence of physicomecanical properties of polyurethane SKU-V on initial relationship/ratio of TDI/polyester: 1 - breaking strength; 2 - relative elongation.

Key: (1). Relative elongation. (2). Breaking strength, kgf/cm^2 . (3). TDI/polyester, mole/mole.

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Further increase in the denseness of cross-linking (decrease M_c from 5300 to 2100) leads to an increase in the module/modulus, which indicates the prevailing effect of primary cross connections on a change in the mechanical properties. During the study of mechanical properties, it is polyurethane on the basis of polyesters, TDI and trimethylol propane it was observed the extreme dependence of breakdown stress from the degree of reticulation, determined experimentally [130], (Fig. 85), which will agree with other data [1, 118].

We consider that, explaining the extreme dependence of mechanical properties on network density, it is necessary to consider a change in the flexibility of chains from network density. So, with large ones M_c , when the flexibility of the cuts between network points is great, is possible the approach of the cuts of chains and the formation of a large number of molecular bonds because of the presence in polyurethane of the polar groups of different types. Obviously, with large ones M_c , when the contribution of secondary bonds to common network density is polyurethane on the basis of polyesters it is great [118], the mechanical properties of these polyurethanes will be determined mainly by the concentration of molecular bonds (Table 52).

Table 51. Effect of maturing degree on the properties of polyurethane elastomers on the basis of polyesters.

(1) M_c элас- томера	(2) Предел проч- ности при растяжении, кг/см ²	(3) Относитель- ное удлине- ние при раз- рыве, %	(4) Остаточное удлинение, %	(5) Модуль уп- ругости при 100%-ном уд- линении, кг/см ²	(6) Предел проч- ности на раз- рыв, кг/см ²	(7) Твердость по Шору (шкала В)
2100	126.0	170	0	38.9	5.4	57
3100	122.5	200	0	29.4	4.5	53
4300	101.5	280	0	21.0	5.4	49
5300	196.0	350	0	18.9	5.4	46
7100	315.0	410	0	23.1	7.2	51
10 900	392.0	490	5	32.2	10.8	55
21 000	385.0	510	10	35.0	25.2	56

Key: (1). elastomer. (2). Tensile strength, kg/cm². (3). Elongation at rupture. (4). Residual, elongation. (5). Module/modulus of elasticity during 100o/o elongation, kg/cm². (6). Limit of strength to tear, kg/cm². (7). Shore hardness (scale B).

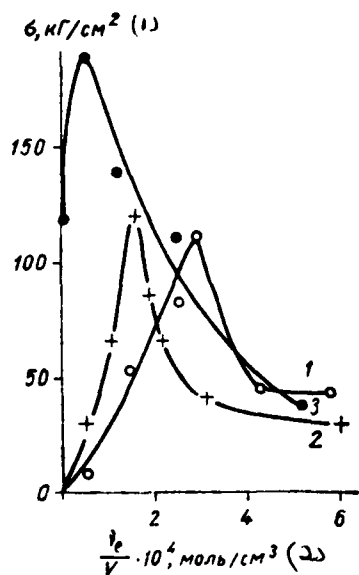


Fig. 85. Dependence of breakdown stress from degree of reticulation:

1 - Polydiethylenesuccinate urethane; 2 - Polydiethyleneadipate urethane; 3 - Polydiethylenesebacate urethane.

Key: (1) . kgf/cm². (2) . mole/cm³.

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Decrease M_c leads to a reduction in the flexibility of the cuts of chains and an incidence/drop in the number of secondary bonds in common/general/total network density. Further increase of the number of nodes in grid because of the introduction of the trifunctional crosslinking agent so decreases the flexibility of the cuts between nodes, that a quantity of secondary cross connections very falls. The dominant role from this point on, belongs to the chemical cross connections an increase in quantity of which contributes to an increase in module/modulus [287].

The comparison of the data of Table 51 and 52 shows that value M_c it is polyurethane the basis of different polyether/polyesters it dissimilarly affects their mechanical properties. So, dependence on M_c the module/modulus of hardness, elongation at rupture in range from 2000 to 5000-6000 is identical for simple and polyesters. At the same time, if in the case of polyesters tensile strength with change M_c from 2000 to 3000 decreases, then for polyethers - it leads to an

increase in the tensile strength. This can be bonded with the fact that in elastomers the basis polyethers the intermolecular forces do not play this role as in elastomers the basis of the polyesters in which the presence of carbonyl group contributes to the emergence of a large quantity of molecular bonds.

Sometimes the dependence between the structure and properties it is polyurethane on the basis polyethers the same as for polyesters, which was observed during the study of the interrelation of structure and properties of the elastomers from prepolymer on the basis of poly-1,4-hydroxybutyleneglycol, solidified by aromatic diamines [163, 164].

Table 52. Effect M_c on the mechanical properties of elastomers on the basis of prepolymers from poly-1,4-hydroxybutyleneglycol and diisocyanate with a molecular weight of approximately 2000, solidified by the mixtures of diol and triol.

(1) Количество отвердителя на 1 г-экв. форполимера	M_c	(2) Предел прочности при растяжении, кг/см ²	(3) Относительное удлинение при разрыве, %	(4) Модуль упругости при сдвиге при 100%-ной деформации, кг/см ²	(5) Твердость по Шору (шкала А)	(6) Прочность на разрыв по Грейсу, кг/см ²
Гексантириол 1.0 (7)	2090	33.2	235	17.50	55	8.1
Полиоксипропилен-триол (М-700) (8) 1.0	3700	38.8	380	11.90	43	7.2
ПТ 0.6 + пентадиол 0.4 (9)	5800	66.6	645	7.35	38	15.1
ПТ 0.6 + полиоксипропиленгликоль (М-425) 0.4 (10)	6150	93.8	625	5.60	37	11.7

Key: (1). Quantity of hardener on 1 gram equivalent of prepolymer.

(2). Tensile strength, kg/cm². (3). Elongation at rupture. (4). Shear modulus during 100% strain, kg/cm². (5). Shore hardness (scale A).

(6). Strength to tear per Grace, kg/cm². (7). Hexanetriol. (8). Polyoxipropylene triol. (9). pentanediol. (10). Polyoxypropyleneglycol.

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With an increase in the portion/fraction of aromatic part, such elastomers acquire the large part of the strength because of molecular bonds similar to elastomers on the basis polyesters.

During the determination of the modulus of elasticity of expanded polyurethanes on the basis of simple (POPG) and complex (polyesteradipate) polyether/polyesters depending on M_c [176] it turned out that the character of a change of the module/modulus with network density in both cases was identical. At the same time, at one and the same temperatures expanded polyurethanes on the basis of polyester possess greater strength during compression and large modulus of elasticity, than expanded polyurethanes on the basis polyethers, which, in addition is caused by different quantity of molecular bonds during the utilization of polyether/polyesters of different nature.

Is investigated the effect of the degree of cross-linking, calculated theoretically and by that determined experimentally, to some physicomachanical properties of polyurethane coatings [53, 90, 100, 102-104, 119-123]. Table 53 gives the dependence of the properties of polyurethane coatings for the basis of the copolymer of tetrahydrofuran with 250/0 of oxide of propylene (mol. weight 1200) and of adduct of TDI and trimethylol propane on value M_c by that designed theoretically by method of Sandridge [302]. Here are represented the results of the calculation of the concentration of urethane [U] and uric [M] groups under the assumption that the

isocyanate groups react with the formation only of urethane and uric bonds [259].

The dependence of some physicommechanical characteristics of polyurethane coatings on the basis of copolymer indicated previously, adduct, but with the addition 500/0 trimethylolpropane [122] is shown on Fig. 86.

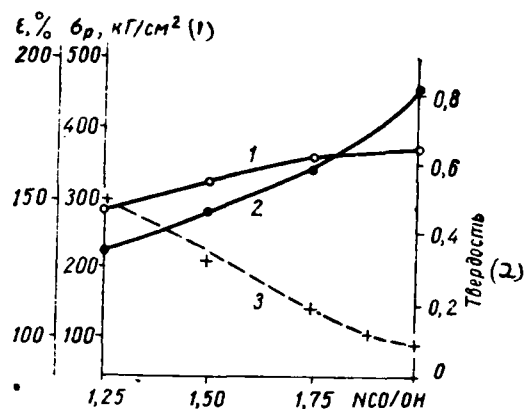


Fig. 86. The dependence of strength with the break (σ_p), of ultimate elongation (ϵ) and relative hardness of coatings on relationship/ratio NCO/OH: 1 - relative hardness; 2 - breaking strength; 3 - ultimate elongation.

Key: (1). kgf/cm². (2). Hardness.

Page 160a.



Fig. 78. Structure of cross-linked polyurethane, obtained from macro-diisocyanate on basis PPG-500 with 80°C.

Page 160b.

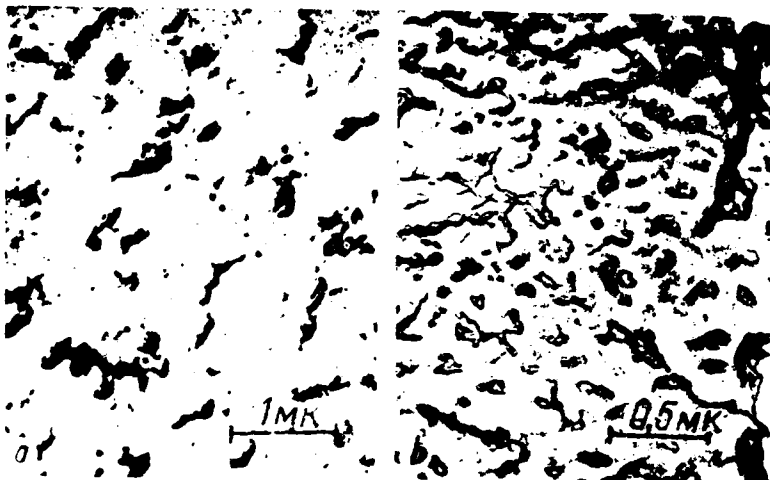


Fig. 79. Structure of cross-linked polyurethane on basis of PPG-2000 at 60° (a) 125°C (b).

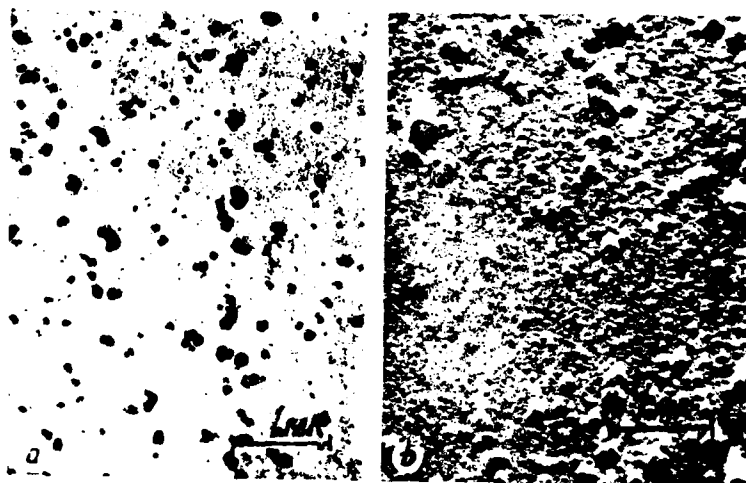


Fig. 80. Structure of specimen/samples of cross-linked polyurethane on basis PPG-1000 (a) and PMG-1000 (b) at 80°C.

Page 160b.

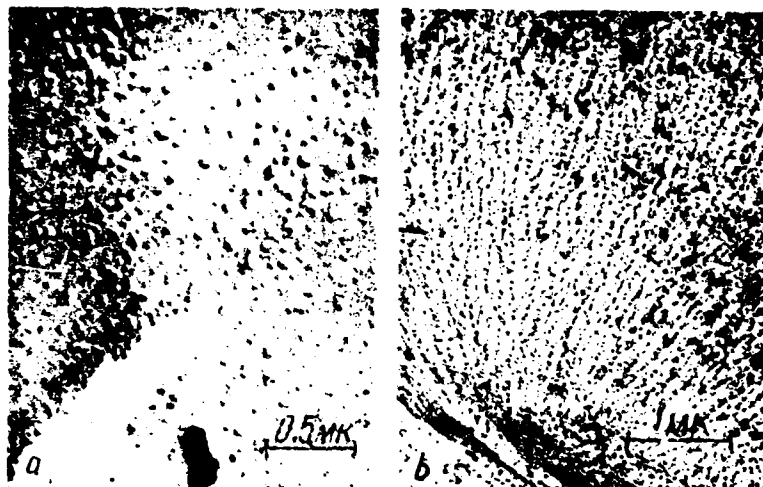


Fig. 81. Structure of cross-linked ones it is polyurethane on basis of esterdiol of different molecular weight ($t=80^{\circ}\text{C}$):.

a - $M_c \sim 10000$; b - $M_c \sim 1000$.

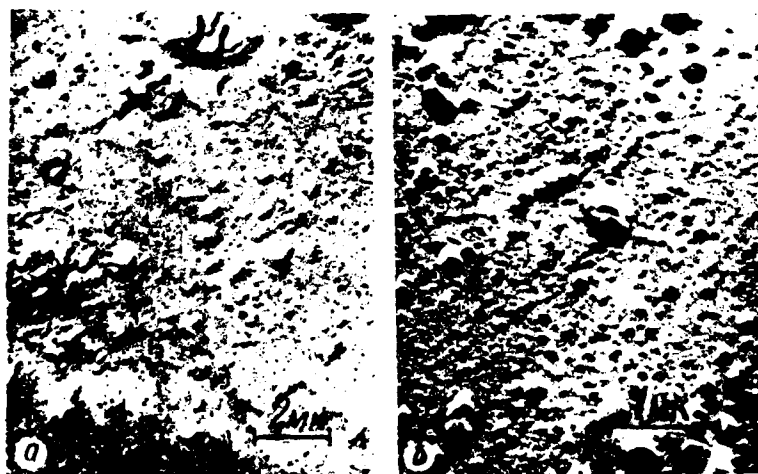


Fig. 82. Structure of cross-linked ones it is polyurethane, obtained by single-stage (a) and two-stage method (b).

Page 160c.

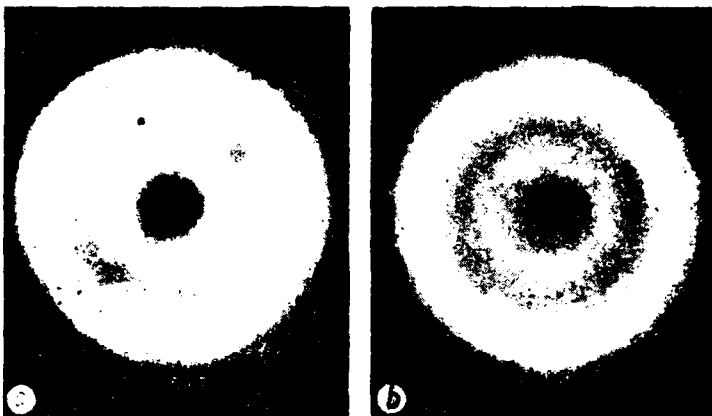


Fig. 104. X-ray photograph of polyurethane on basis of polydiethyleneglycoladipate: a) before stretching; b) after stretching to 1000/o.

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The last component is introduced for reducing the excess of isocyanate groups in the initial compositions.

The given results tell about the fact that an increase in the network density of polyurethane coatings on the basis of simple oligoester causes a monotonic increase in hardness and strength of coatings, decreasing in this case relative elongation.

For coatings on the basis of complex [102] and silicon-bearing oligoester, the character of a change in the physicomechanical properties with network density is analogous such for coatings on the basis of simple oligoester (Table 54, Fig. 87).

Table 53. Physicomechanical properties of polyurethane coatings on the basis of the copolymers of tetrahydrofuran with oxide of propylene and adduct of TDI and TMP.

(1) Состав полиэфирагликоля	NCO/OH	(2) [N] · 10 ² , мол/г	(3) [N] · 10 ² , мол/г	(4) M _c расчетное	(5) Относительная твердость по М-3	(6) Прочность при разрыве (20°С), кг/см ²	(7) Удлинение при разрыве (20°С), %
ТГФ — П-1400 — 25% ОП	2:1	2.33	0.36	4400	0.18	120	660
	3:1	2.53	0.63	3900	0.40	250	390
	4:1	2.66	0.79	3400	0.45	320	350
ТГФ — П-1400 — 15% ОП	2:1	2.37	0.39	4300	0.14	107	766
	3:1	2.56	0.64	3800	0.30	225	289
	4:1	2.69	0.80	3300	0.40	260	241

Key: (1). Composition of polyesterglycol. (2). mole/g. (3). calculated. (4). Relative hardness on M-3. (5). Strength with break (20°C), kg/cm². (6). Ultimate elongation.

Table 54. Physicomechanical properties of the polyurethane coatings containing silicon.

(1) Состав композиции	NCO/OH	(2) [N] · 10 ² , мол/г	(3) [N] · 10 ² , мол/г	(4) M _c вычисленное	(5) Относительная твердость по М-3	(6) Прочность при разрыве (20°С), кг/см ²	(7) Удлинение при разрыве (20°С), %
(CH ₃) ₂ Si(OCH ₂ CH ₂ OH) ₂ + — аддукт бисуретовой структуры (7)	1.00	—	—	1580	0.56	160	106.0
	1.25	3.42	1.57	1443	0.72	247	35.4
	1.50	3.00	1.99	1320	0.81	427	31.2
	1.75	2.70	2.69	13	0.85	500	29.0
	2.00	2.45	2.43	1230	0.85	525	27.0
C ₂ H ₅ Si(OCH ₂ CH ₂ OH) ₃ + тот же аддукт (8)	1.00	—	—	720	0.64	—	—
	1.25	2.85	2.14	665	0.73	325	29.0
	1.50	2.50	2.50	627	0.86	516	27.0
	1.75	2.22	2.79	600	0.91	535	26.0
	2.00	2.00	3.00	530	0.86	580	31.0
Si(OCH ₂ CH ₂ OH) ₄ + тот же аддукт (9)	1.00	—	—	550	0.66	80	202.0
	1.25	2.53	2.46	560	0.82	487	27.0
	1.50	2.20	2.79	570	0.84	626	27.0
	1.75	1.95	3.04	579	0.86	650	32.0
	2.00	1.75	3.29	586	0.78	—	—

Key: (1). Composition of composition. (2). mole/g. (3). calculated.
(4). Relative hardness on M-3. (5). Strength with break of kg/cm².
(6). Ultimate elongation. (7). adduct of biuret structure. (8). the same adduct.

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An increase of the quantity of chemical nodes in the three-dimensional/space grid of polyurethane is led to a certain degree for the decrease of the effect of physical bonds on mechanical properties it is polyurethane. Therefore if for elastomers on the basis of complex and simple oligoester with large ones M are observed differences in a change of physicochemical property with change M , to certain limit, then with further decrease M , when the

contribution of physical bonds to common/general/total network density becomes less, these differences are smoothed. It is obvious, on the same reason for the coatings where the effective density of cross-linking is much more than in elastomers, it is not noticed essential differences in the character of a change in the basic mechanical properties with network density during the utilization of oligoester of different nature.

Thus, the degree of reticulation determines to a considerable extent the physicommechanical properties of polymers. Another important factor, especially with increased temperatures, is the nature of cross connections in three-dimensional/space grid it is polyurethane, that depends on the hardener used. As a result of the investigation of effect, it is diamine [274] and water [279] as the hardeners to the properties of polymers on the basis of different diisocyanates it is establish/installed (Table 55), that strong intermolecular interaction in polymers leads to the fact that the elastomer acquires the high values of module/modulus and strength for tear as a result of forming the ureic groups during solidification by diamines.

The presence of rigid segments in chain (bulky aromatic diisocyanates and aromatic diamines, used as hardener) also provides the high values of module/modulus and strength for tear. The presence

of pliable groups in hardener, for example thioester, lowered tensile strength, strength to tear, module/modulus and hardness.

Consequently, application/use it is diamine as hardeners is led in a number of cases to an improvement in the mechanical properties as a result of the formation of strongly polar uric groups.

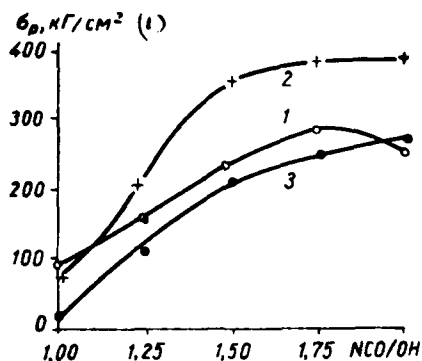


Fig. 87. The dependence of the breakdown stresses of free films on the basis of oligodiethyleneglycoladipate (ODA) from relationship/ratio NCO/OH: 1 - ODA-400; 2 - ODA-600; 3 - ODA-800.

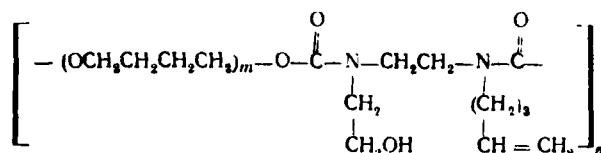
Key: (1). kgf/cm².

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Investigated [by 227] the effect of structure it is diamine, in particular quantity of carbon atoms in them, to the mechanical properties of the polyester-urethane fibers, obtained on the basis of complex oligoester (oligoethyleneglycoladipate with a mol. weight of 2000) and of diphenylmethane diisocyanate. Fibers developed rubber-like properties, in spite of the absence of chemical cross connections, which is caused by the formation of the sufficiently strong/durable grid of physical bonds. The fibers, obtained on basis

it is diamine with the odd number of atoms of carbon (Fig. 88), they have higher breaking strength and greater elongation; reverse picture is observed for a module/modulus. It is possible to assume that this abrupt change in the properties it is polyurethane with the content of a number of carbon atoms bonded with the formation of different number of secondary physical bonds in the polymers being investigated in the case of even and odd quantities of carbon atoms in diamine. For proof of this, are necessary further investigations with the attraction of the fine/thinner physicochemical methods of studying the structure of polymers.

Claff and Glading [187] investigated effect of the type of cross connections on the properties of urethane elastomers on the basis of simple oligoester. The studied linear polyurethane



are synthesized from bis-chloroformate of poly-1,4-hydroxybutyleneglycol and N-2 hydroxyethyl-1-pentaneylethylenediamine.

Table 55. Effect of hardeners on the properties of polyurethane elastomers.

(1) Отвердитель	(2) Предел прочности при растяжении, кг/см ²	(3) Относительное удлинение при разрыве, %	(4) Модуль упругости при 300%-ном удлинении, кг/см ²	(5) Предел прочности на разрыв, кг/см ²	(6) Эластичность, %	(7) Твердость по Шору (шкала А)
(8) 2,4-Толуиленидиизоцианат						
Дианизидин (9)	273.0	635	31.5	182.0	57	58
2,4-Толуиленамин (10)	280.0	720	35.0	143.5	51	60
Вода (11)	199.5-248.5	730	—	82.5	—	—
(12) Гексаметилендиизоцианат						
4,4'-Диаминодифенилметан (13)	269.5	680	80.5	210.0	53	90
Дианизидин (9)	217.0	650	50.3	101.5	53	77
2,4-Толуиленамин (10)	266.0	710	39.9	143.5	57	69
2,4-ГДА	126.0	707	25.9	112.0	54	70
Вода (11)	234.5	1000	—	57.5	2	—

Note. Last/latter two polymers are obtained on the basis of poly-1,2-propyleneadipate, remaining - on the basis of polyethyleneadipate; molecular weight of both of polyesters is equal to 2000.

Key: (1). Hardener. (2). Tensile strength, kg/cm². (3). Elongation at rupture. (4). Module/modulus or elasticity during 300o/o elongation, kg/cm². (5). Limit of strength to tear, kg/cm². (6). Elasticity. (7). Shore hardness (scale A). (8). Toluenediisocyanate. (9). Dianisidine. (10). Toluenediamine. (11). Water. (12). Hexamethylene diisocyanate. (13). Diaminodiphenylmethane.

As the acceptor of acid, is undertaken the water/aqueous carbonate of sodium. In the molecules of such polymers two reactive centers, because of which can be formed the cross connections: the lateral hydroxyl groups, capable of interacting with isocyanates, and the lateral vinyl, which enter in reaction with gray. With the synthesis of the three dimensional polymer, were used following hardeners: 3,3'-dimethoxy-4,4'-biphenyldiisocyanate; prepolymer with terminal isocyanate groups (mol. weight 5000), obtained during the reaction of 4 moles of poly-1,4-hydroxybutyleneglycol (mol. weight 1000) and 5 moles of 3,3'-dimethoxy-4,4'-biphenyldiisocyanate; the sulfur-containing mixture.

It was established that the module/modulus, hardness and elasticity depend either on chemical nature or on the length of chain of hardener. However, with the same density of cross connections, measure of contraction during compression (22 h at 70°C and 70 h with 100°C) for the elastomers, solidified gray, is higher than in the elastomers, solidified by isocyanate. This difference is bonded with the fact that the cross connections, formed because of sulfur, especially disulfide type bond, are less thermostable, than urethane type bond. The type of cross connections has small effect on mechanical properties it is polyurethane at room temperature [228, 317].

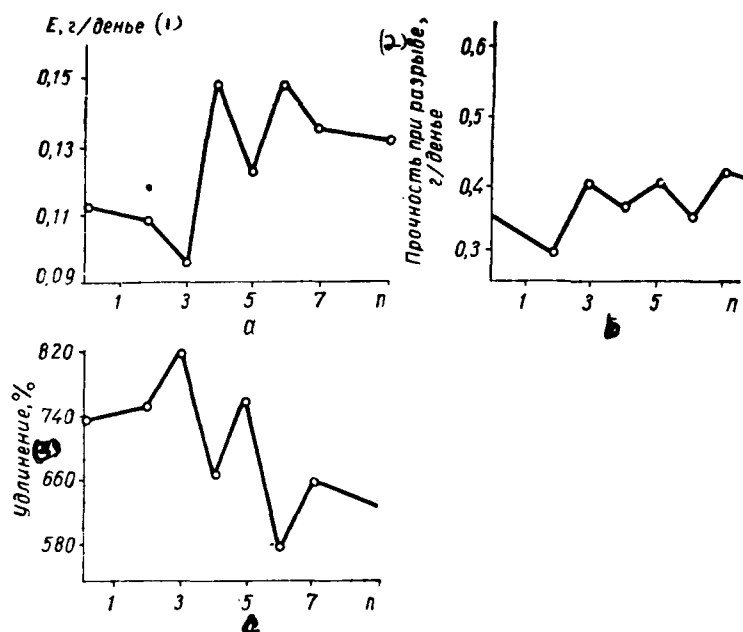


Fig. 88. Effect of a number of atoms (n) of carbon in diamine on the module/modulus of elasticity during 300% elongation (a), strength (b) and ultimate elongation (c) of polyurethane fibers.

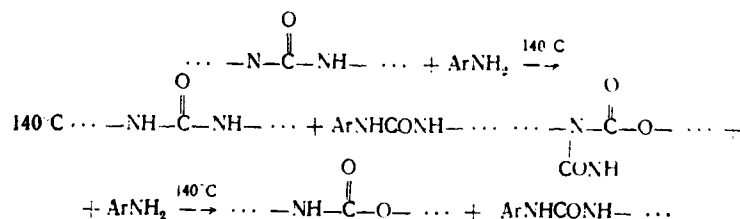
Key: (1). g/denier. (2). Strength with break, g/denier. (3). Elongation.

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On the other hand, the melting point of polymers is above, if cross connections are formed because of triol or triisocyanate, and it is below, if cross-linking goes because of the excess of

The effect of ne-thermostable biuret and allophanate bonds on some properties it is polyurethane shown for the example of the spongy materials, which contain 90, 100 and 120o/o of diisocyanate (isocyanate index with respect 90, 100, 120) from that required at the designed values M_c from 600 to 1730 [302].

It is established/installed, that the spongy materials with index 120 disintegrate with aniline with 140°C much faster than with index 90-100. To the reactions or the destruction of allophanate and biuret groups can be represented in the following diagram:



After the processing/treatment by aniline, the spongy materials with index 120 much more strongly will swell in dimethylacetamide (DMA) with 25°C, than polyurethane with index 90 and 100, which indicates more rapid destruction of cross connections in spongy material with index 120.

These results are closely related to the character of the curves of modulus of torsional shear for the same spongy materials (Fig. 89). The spongy materials with isocyanate indices 90 and 100, which contain a very small quantity of uret or allophanet groups, have relatively flat curve changes in the module/modulus up to temperature of 160-170°C. In the case of expanded polyurethanes with index 120, is observed the break for curve and sharp lowering in the module/modulus with 110-130°C.

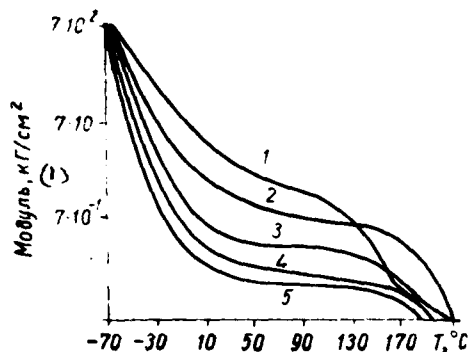


Fig. 89. The curves of the dependences of modulus of torsional shear on temperature for expanded polyurethanes on the basis polyethers: 1 - isocyanate index 120; $M_c = 680$; 2 - isocyanate index 100, $M_c = 1100$; 3 - isocyanate index 120, $M_c = 1350$; 4 - isocyanate index 100, $M_c = 1600$; 5 - isocyanate index 90, $M_c = 2000$.

Key: (1). Module/modulus, kgf/cm².

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It is assumed that the latter is caused by the destruction of allophanate or biuret groups. According to [249] the dissociation of allophanates becomes noticeable already at temperature of 106°C.

It is investigated [287] the dependence of modulus of torsional shear on temperature it is polyurethane on the basis of polyethyleneglycoladipate, cross-linked with trimethylol propane and

solidified by different mixtures of trimethylol propane (TMP) and of aromatic glycol multirathane X (Fig. 90). The modulus of elasticity of the specimen/sample, which does not contain chemical cross connections (curve 1), has the high value with 25°C, but rapidly it decreases at 130-150°C. During replacement by 70o/o of diol by triol (curve 2) the modulus of elasticity at room temperature is less and insignificantly it is changed with an increase in the temperature to 170-190°C. The full/total/complete replacement of diol by triol leads to even greater expansion of the temperature interval, by which occurs lowering the module/modulus (curve 3).

The observed character of a change in the module/modulus with temperature is explained by the fact that the secondary physical bonds much more easily disintegrate under the action/effect of heat, than primary valence ones. The elastomer, which has is many physical bonds (curve 1), it is more strong/durable and it is harder at room temperature, but its stability is lower than in the polymer, cross-linked with triol.

For it is polyurethane the mark/brand Durethane U, obtained on the basis of hexamethylene diisocyanate and butanediol-1,4 [204], is observed a significant incidence/drop in the module/modulus with temperature, especially after 80°C, which is explained by destruction physical and, possibly, weak chemical, the type of allophanate bonds

(Fig. 91). Thermoplastic polyurethane of another nature [270, 342] possess excellent properties at low temperatures - high wear resistance, stability to the action/effect of ozone, radiation, oils, aliphatic solvents. At high temperatures in these, it is polyurethane considerably they deteriorate mechanical properties as a result of the dissociation of physical bonds. For their improvement is recommended the vulcanization with peroxides and epoxies.

Consequently, the physicommechanical properties it is polyurethane they are determined to a considerable extent by the type of the bonds, which compose three-dimensional/space grid.

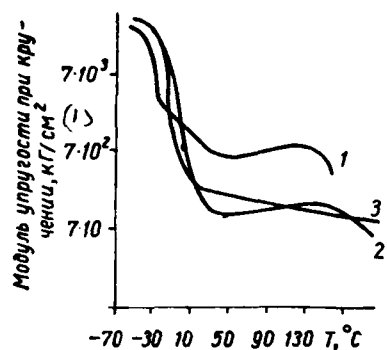


Fig. 90. The dependence of modulus of torsional shear on temperature for elastomers on the basis of polyethyleneglycoladipate and diphenylmethane diisocyanate: 1 - 0o/o of TMP; 2 - 70o/o of TMP; 3 - 100o/o of TMP.

Key: (1). Modulus of torsional shear, kgf/cm².

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Especially sharply is developed the dependence of properties it is polyurethane on the nature of bonds with an increase in the temperature.

The structure of the three-dimensional grid of polyurethane is determined by synthesis conditions for polymer. For example, the formation of grid will occur differently in the case of obtaining polyurethane by mono- and two-stage method. During formation through

the stage of prepolymer (two-stage method) it is possible to expect the emergence of more regular grid which must lead to an improvement in the properties of polymers. So, during the investigation of the properties of elastomers on the basis of polyoxypropyleneglycol, TDI and 3,3'-dichloro-4,4'-diaminodiphenylmethane (MOSA), obtained by prepolymer and single-stage method [166], it turned out that the first have greater tensile strength, but smaller strength to tear, module/modulus of elasticity, elasticity and contraction during compression.

The polyurethane coatings on the basis of polyesters, synthesized by single-stage method with 20°C, had smaller hardness than obtained through the prepolymer (adduct of trimethylol propane with TDI) [100]. But at the higher temperature of solidification these differences disappeared.

The polyurethane elastomers on the basis of polyesters, synthesized by prepolymer method [290], had smaller hardness and tensile strength, than obtained by single-stage method. Especially noticeably the method of synthesis was reflected in the melting point which proved to be considerably above in the case of "single-stage ones" was polyurethane. This gave the basis to the authors to draw a conclusion about the greater degree of the crystallinity of these polymers.

As can be seen from the comparison of data on the effect of the method of synthesis on properties it is polyurethane, it is difficult to draw a simple conclusion about the advantages of that or another method. It is obvious, necessary the additional experimental investigations in this direction, which make it possible to explain the effect of the method of obtaining on the structure of the three-dimensional grid of polyurethane and, in connection with this, to their physicommechanical properties.

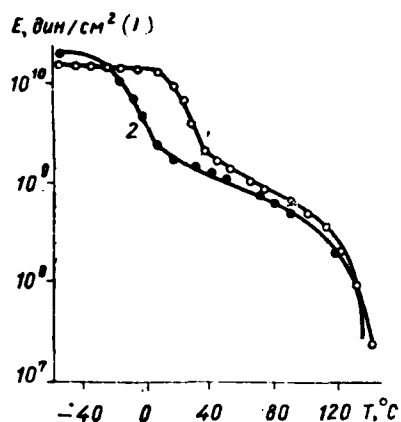


Fig. 91. The dependence of the modulus of shear of polyurethane of the mark/brand "Durethane" U on the temperature: 1 - the additionally dried out specimen/sample with 29°C; 2 - specimen/sample, saturated by 40/o of water and then dried out at 4°C.

Key: (1) . dyn/cm².

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The results of the investigation of the effect of the nature of components on structure and properties of polyurethane indicate that the physicochemical properties of these materials, just as other polymers, are determined by molecular weight of initial components, by effectiveness of intermolecular interaction, by hardness of the segments, which compose polymer chains. Polyurethane can be considered as block copolymers [307] with the soft segments of simple or polyester and the rigid segments, formed by urethane or urea urethane blocks. Soft segments condition an increase in the elasticity and ultimate elongation. An increase in the concentration of rigid segments contributes to strengthening intermolecular interaction and therefore raises the hardness of polyurethanes, their strength by break, melting points and vitrification, but decreases elasticity and ultimate elongation. A change in the nature of soft and rigid segments and type of cross connections makes it possible to obtain polyurethane materials with the assigned properties.

TEMPERATURE DEPENDENCE OF SOME PROPERTIES OF POLYURETHANES.

The examination of some physicochemical properties of the polyurethane elastomers and other materials showed that they develop the series/number of the specific properties, which differ them from other polymers. However, the reasons for specificity, until now, are investigated very little. From this point of view interesting to study the temperature dependence of some properties it is polyurethane in solution and block. It is important to also explain a question concerning what properties of the isolated/insulated macromolecules are transmitted to polymeric body and as this occurs.

It is reveal/detected that in polymers besides the basic transitions, bonded with vitrification, there are additional temperature transitions, which are developed in the form of the anomalies of the temperature dependence of some properties [138, 139, 152, 197, 209, 295, 301, 331, 342]. This type of transitions are reveal/detected both in the pure/clean polymers and in solutions [139, 152, 209, 295]. So, the additional conformational transition of polystyrene in block is revealed in the form of the washed away maximum of approximately 50°C in the curve of differential-thermal analysis [344]; a sharp incidence/drop in the internal pressure (i.e. energy of cohesion) [301]; increase in the Bragg distances between phenyl groups [246]; break on dilatometric straight lines [197]. In solutions analogous transitions were detected in the form of an anomalous dependence of intrinsic viscosity and size/dimensions of

balls [152, 295]; the dielectric power factor [138, 139]; incidence/drop in the anisotropy of chain with temperature [152]; the jump of surface tension [209].

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For ether/esters or cellulose, is found the collection of transition temperatures and the conclusion is made that the latter are caused by a change in the molecular mechanism of the motion of macromolecules [197]. So, the lowest temperature of transition answers a minimum number of possible conformations, and in proportion to an increase in the temperature a number of conformations and free space are increased by cooperative method, i.e., these transitions can be considered as conformational.

Is made the attempt to connect temperature transitions in dilute solutions, reflecting conformational transformations in the isolated/insulated macromolecules, with temperature transitions in polymeric block, that bear cooperative character [95]. The authors tried to reveal/detect conformational transitions for was polyurethane different type. It was assumed that the presence in the polyurethane chain of two types of sections (pliable ether/ester or glycol component and rigid urethane groups), capable of forming intra- and intermolecular hydrogen bonds, must in a specific manner

affect the temperature dependence of some properties of polymers. Are carried out dilatometric measurements, differential-thermal analysis, and is also measured the characteristic viscosity of the solution of some polyurethanes.

Are investigated two specimen/samples of prepolymers on the basis of polydiethyleneglycoladipate (mol. weight 1600 and ⁴¹⁰⁰~~1400~~) and of mixture of isomers 2,4- and 2,6-TDI (corresponding mol. weight it is polyurethane 3200 and 13 500), and also polyurethane on basis of 1,4-butanediol and 2,4-TDI (2,4-PU, mol. weight 9000). Are measured volumetric expansion coefficients for the first two specimen/samples in benzene, methylethylketone (MEK) and in these solvents with the addition of dichloroacetic acid (DKhUK) and also in pure DKhUK (Fig. 92, Tabl. 56). For 2,4-PU as solvents, are undertaken cyclohexanone, dimethyl formamide (DMF) and their mixtures with DKhUK (Fig. 93). Volumetric expansion coefficients were calculated from the formula

$$\alpha = \Delta V / V_0 \Delta T, \quad (\text{VII}, 1)$$

where $\Delta V = V_{\text{раствора}} - V_{\text{растворителя}}$; V_0 — an original volume of polymer in solvent; ΔT — difference in temperatures $T - T_0$.

Table 56. Volumetric expansion coefficients (α) it is polyurethane.

(1) Растворитель	(2) М полиэ- фирной компонен- ты	α	(3) Растворитель	М полиэ- фирной компонен- ты	α
(4) Бензол	1600	0.00065	МЭК	4100	0.0107
	4100	0.00100	МЭК + ДХУК	1600	0.0077
(5) Бензол + ДХУК	1600	0.00084		4100	0.0095
	4100	0.00193	ДХУК	1600	0.0026
(6) МЭК	1600	0.00770		4100	0.0047

Key: (1). Solvent. (2). M of polyether/polyester component. (3). Solvent. (4). Benzene. (5). Benzene + DKhUK. (6). MEK.

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For the same specimen/samples are taken the curves of the differential-thermal analysis (Fig. 93).

As can be seen from Fig. 92, for solutions it is polyurethane an increase in the volume of the dissolved polymer it occurs linearly in all cases. The calculated value α (see Table 56) increases in all solvents with an increase in the length of polyether/polyester component. Value α in MEK two times more, in comparison with benzene, which, probably, is bonded with the quality of solvent. MEK is poor solvent for it is polyurethane [95]; therefore in it an increase of the volume of polymer with temperature must be more than in benzene

(good solvent). Addition of DKhUK, with capable of the formation of hydrogen bonds, does not lead to change α in MEK. This it is possible to explain by the small contribution of the urethane groups, which condition the appearance of hydrogen bonds. Really/actually, value α in benzene is close to the same for pure/clean polyesters of different structure ($\alpha=0.00074-0.00084$ with mol. weight 790-2200). The addition of DKhUK into benzene makes solvent worse, since DKhUK itself - a poor solvent for is polyurethane.

Thus, for it is polyurethane with a small concentration of urethane groups (three or four to one molecule of polyurethane with a mol. weight of 13 500) the possible destruction of hydrogen bonds does not virtually affect a change of the volume of polymer in solution, but difference in α for different solvents, probably, it depends on a quantity of latter.

For polyurethane 2,4-PU, the picture of dilatometric measurements in different solvents is dissimilar (see Fig. 93).

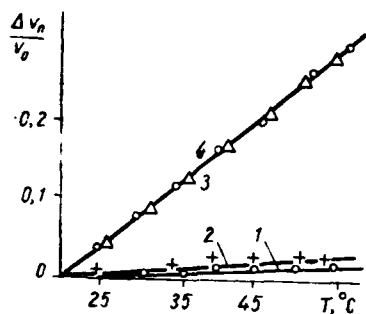


Fig. 92.

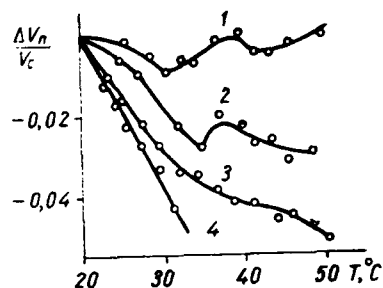


Fig. 93.

Fig. 92. Dependence $\Delta V_n/V_0$ on temperature for prepolymers on basis of polydiethyleneglycoladipate (mol. weight 1600) and of TDI:

1 - in benzene; 2 - in benzene with addition of DKhUK; 3 - in MEK; 4 - in MEK with addition of DKhUK.

Fig. 93. Dependence $\Delta V_n/V_0$ on temperature for polyurethane on basis of 1,4-butanediol and 2,4-toluenediisocyanate:

1 - in cyclohexanone; 2 - in DMF; 3 - in cyclohexanone with addition of DKhUK; 4 - DMF with addition of DKhUK.

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From curved $\Delta V/\Delta V_0$ from T in cyclonexanone and DMF is visible explicit conformational transition of approximately 40°C. In this case the concentration of urethane groups in chain is considerably higher than in preceding; therefore their effect on the properties of polyurethane must be significant. Since the addition into cyclohexanone and DMF of the dichloroacetic acid, capable of the formation of hydrogen bond, leads to the disappearance of the conformational transition, which exists in pure/clean solvents with 40°C. it is possible to assume that it is caused by the break of hydrogen bonds. The data of the differential-thermal analysis (Fig. 94) indicate also the conformational transition in region of 40°C in all cases for this polymer, while for pure polyether/polyesters of the same it is not observed. It is characteristic that the analogous transition is observed also in block polymers (Fig. 94, curves 7, 8).

The thermomechanical investigation of elastomers on the basis of polyethyleneglycoladipate with chain length greater than their mechanical segment, and toluenediisocyanate, also shows that with $T \sim 40^\circ\text{C}$ begins the irreversible strain. The dependence of intrinsic viscosity $[\eta]$ of 2,4-PU on the temperature in cyclohexanone shows that in region of 40-50°C ductility/toughness/viscosity sharply is lowered, and this, probably, it is bonded with the break of

intramolecular hydrogen bonds. Increase η_{sp}/c during dilution, according to [327], is bonded with the dissociation of hydrogen bonds.

From aforesaid it follows that the conformational transition in region of 40-50°C is caused by the break of hydrogen bonds, which occurs in dilute solutions and block.

Both in the solution and in block besides transition in region of approximately 40°C for 2,4-PU are observed additional maximums in region of 10-12° and by 20°C. However, in pure/clean DMF and in cyclohexanone with the addition of DKhUK transition with 20°C disappears, while at 10-12°C it is retained. For solutions of PU in benzene with 25°C, also occurs the transition, but in pure/clean PU it is absent. The presence of these transitions, probably, is caused by the manifestation of the mobility of other components of urethane chain (besides urethane groups).

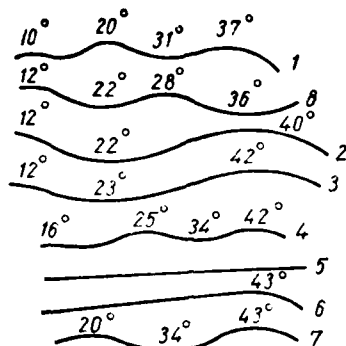


Fig. 94. Thermograms of heating: 1 - 2,4-PU in cyclohexanone; 2 - 2,4-PU in DMF; 3 - 2,4-PU in cyclohexanone with addition of DKhUK; 4 - PU in benzene; 5 - PDEGA; 6 - PU; 7 - 2,4-PU; and thermogram of cooling 2,4-PU in cyclohexanone (numeral in curves they correspond to transition temperatures).

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Differential cooling curve (see Fig. 94, curve 2) for 2,4-PU in cyclohexanone, shows that all processes - both break of hydrogen bonds and other conformational transitions - are reversible.

Thus, the analysis of experimental data makes it possible to make the conclusion that the anomaly of the temperature dependence of

some properties of polymers in block state is closely related to the conformational transitions, which exist in dilute solutions, and is caused by the properties of individual macromolecules.

It is very interesting to compare results presented above with the data of the direct study of the temperature dependence of mechanical properties.

From the classical theory of high elasticity, it is known that for the flexible chains, between which are absent specific reactions, the equilibrium modulus of high elasticity E_{∞} is bonded with molecular weight of the cut of the chain between network points M_c and temperature by the following relationship/ratio:

$$E_{\infty} = 3RT\rho/M_c$$

where R - gas constant, ρ - density. Was investigated the applicability of this equation for describing the properties of some polyurethane elastomers [7]. In the sufficiently wide temperature range, is found the linear dependence of module/modulus on temperature; however, during the extrapolation of experimental direct/straight before intersection with axis temperatures, they do not pass through the origin, as this follows from the equation of kinetic theory, but the transverse axis of abscissas at the temperatures, distant from absolute zero. Consequently, extrapolation

into low-temperature ones region it proves to be not substantiated for it is polyurethane. In general form this can be explained by the fact that lower than vitrification temperature the character of thermal agitations in polymer is analogous to the character of thermal agitations in common solids and it is not bonded with the flexibility of chains. In this temperature range, the strain bears no longer highly elastic, but truly elastic character and, therefore, it cannot be described by the kinetic theory of elasticity. It is possible that the determined according to intersection with the axis of abscissas temperature corresponds to the brittle point of elastomer and can serve as additional characteristic. On the basis of this into equation, it is possible to introduce the correction, which considers the results of the extrapolation of the experimental straight line

$$E_{\infty} = \frac{3RT}{\rho} (T - T_0).$$

The obtained equation is in the best accord with experiment, and parameter T_0 can be connected with brittle point, since the latter begins when completely cease all segmental movements.

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Are establish/installed some temperature anomalies of the mechanical properties of polyurethane rubbers, in which distinctly is

developed the specific character of their behavior [70]. Was investigated temperature dependence of the value of equilibrium highly elastic strain and module/modulus of high elasticity, and also the strength of polyurethane rubbers on the basis of diethyleneglycoladipate of different molecular weights and TDI, cross-linked with triethanolamine and which are characterized by the presence or the absence of plasticizer - dibutylphthalate.

Figure 95 gives the curves of creep of the nonplastic and softened rubbers at different temperatures. The temperature course of these dependences is clearly anomalous, and the minimum value of highly elastic strain is observed at temperature of 35°C for nonplastic and by 40-50°C for that plasticized polymers.

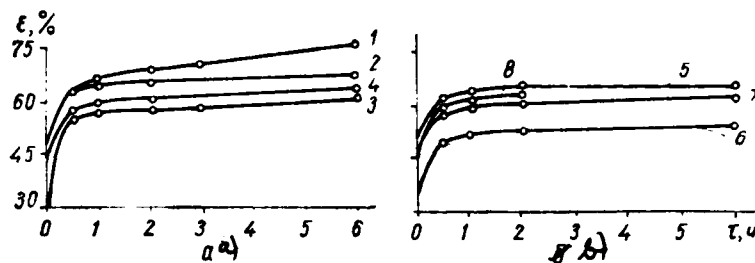


Fig. 95. Curves of creep of the nonplastic (a) and softened^(b) rubber:

1 — 0; 2 — 20; 3 — 40; 4 — 60; 5 — 20; 6 — 35; 7 — 40; 8 — 50° C.

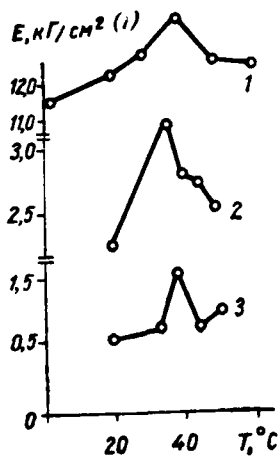


Fig. 96.

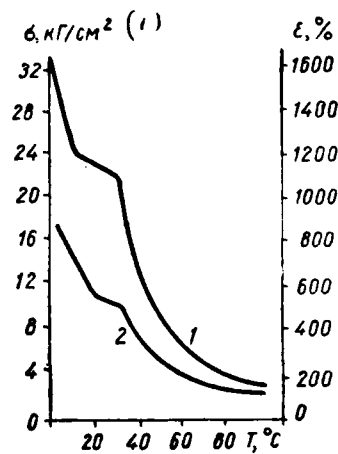


Fig. 97.

Fig. 96. Dependence of modulus of elasticity on temperature: 1 -

M=2500, with plasticizer; 2 - M=1900, without plasticizer; 3 - M=1900, with plasticizer.

Key: (1). G/cm².

Fig. 97. Dependence of strength (1) and of elongation at rupture (2) on temperature.

Key: (1). kg/cm².

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The temperature course of module/modulus also develops anomaly and is characterized by the clearly expressed maximum at temperatures of 35-40°C (Fig. 96). Finally, in the temperature range of 35-40°C are observed extreme points in the curves of the temperature dependence of strength and elongation at rupture (Fig. 97).

According to the classical theory of high elasticity, which in the majority of the cases correctly describes the temperature dependence of the properties of natural and synthetic rubbers, the equilibrium modulus of highly elastic strain must grow/increase with temperature as a result of an increase in the energy of the thermal agitation of chains. At the same time, the amount of equilibrium

strain little depends on temperature.

As can be seen from given data, the value of module/modulus passes through the sharply pronounced maximum, that does not make it possible to characterize the behavior of polyurethane rubbers with the aid of kinetic theory. A change in the mechanical properties (strength and elongation at rupture) also bears nonmonotonic character. The investigation of the temperature dependence of module/modulus for it is polyurethane, obtained on basis polyether/polyesters of different molecular weight, it showed, that the common/general/total anomaly of temperature dependence is retained independent of molecular weight and presence or absence of plasticizers. In this case, the temperature range of the manifestations of anomaly is not changed.

Analogous results are obtained during the study of the temperature dependence of the value of the equilibrium module/modulus of high elasticity for polyurethane elastomers on the basis of polydiethyleneglycoladipate of different molecular weights (Fig. 98). Findings give to us the foundation for considering that the temperature anomalies of mechanical properties it is polyurethane they are bonded with the specific molecular processes, which take place in the temperature range of 40-50°C.

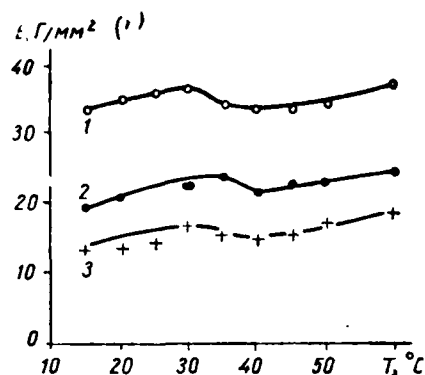


Fig. 98. The dependence of the equilibrium modulus of high elasticity of polyurethane elastomers on the temperature: 1 - on the basis of polydiethyleneglycoladipate (mol. weight 815) and of TDI (crosslinking agent diethylene glycol + glycerin = 1:1); 2 - on the basis of polydiethyleneglycoladipate (mol. weight 1750) and of TDI (crosslinking agent diethylene glycol + glycerin = 1:3); 3 - on the basis of polyethyleneglycoladipate (mol. weight 1000) and of TDI (crosslinking agent diethylene glycol + glycerin = 1:1).

Key: (1) . G/mm^2 .

It is interesting to note also data on the temperature dependence of module/modulus elasticity of the rigid polyurethane films, which are used as protective coatings (Fig. 99). In contrast to elastomers in the initial period of an increase in the temperature, is observed a common for the glassy polymers reduction in the module/modulus with a temperature rise. Further shape of the curve is analogous to shape of the curve, given in Fig. 96.

Thus, in temperature range near 40°C occur changes in the properties, bonded with the conformational transitions, caused by the decomposition of the part of the molecular bonds, first of all hydrogen. The significant contribution to properties is polyurethane it introduces also the reaction between polyether/polyester blocks. Weakening molecular bonds with an increase in the temperature leads to an increase in the mobility of blocks and a manifestation with them their own flexibility.

Thus, the effect of temperature produces change in the total number of intermolecular hydrogen and van der Waals bonds. The decomposition of the grid of these bonds is equivalent to an increase in the distance between the nodes of the three-dimensional/space grid, formed as a result of physical reactions and which plays the dominant role in the properties of polyurethane elastomers [115]. Because of this, and also due to an increase in the mobility of the

cuts of chains occurs the common/general/total increase of the strain in temperature range of higher than 40°C and the bonded with it reduction in the module/modulus.

For the plasticized polymer the region of anomaly is shift/sheared to the side of higher, but lower temperatures, as it could seem at first glance. This is caused by preservation/retention/maintaining in the plasticized polymer of the durable bonds, which are decomposed at higher temperature.

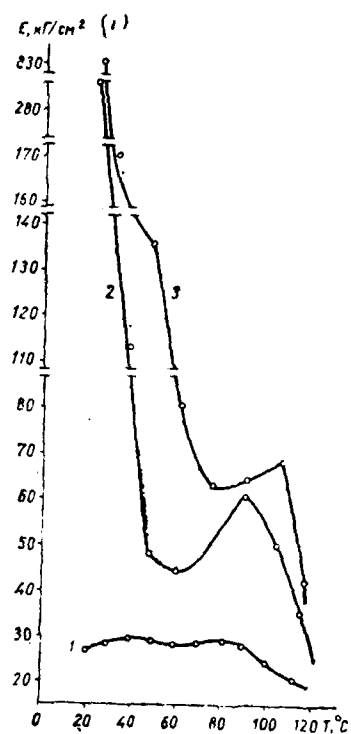


Fig. 99. Dependence of modulus of elasticity of polyurethane films on temperature (NCO/OH=2:1):

1 - on basis of tetrahydrofuran with oxide of propylene and adduct of trimethylol propane with TDI; 2 - on basis of oligodiethylenesuccinate (mol. weight 800), trimethylol propane and TDI; 3 - on basis of oligodiethyleneglycoladipate (mol. weight 800).

Key: (1). kgf/cm².

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Thus, decomposing the grid of physical bonds and caused by this change in the flexibility of the cuts of polymer chains, i.e., the factual rearrangement of the structure of grid with temperature, determine the anomalies of the physicommechanical properties, components the essential feature of polyurethane elastomers. It is completely possible that this mobility of structural grid and lightness/ease of its rearrangement under the effect of external agencies determine many specific properties it is polyurethane.

THERMODYNAMICS OF THE HIGHLY ELASTIC STRAIN OF POLYURETHANE ELASTOMERS.

During the explanation of the bond of the mechanism of strain with the structure of polymer special importance have the cases when very structure of body undergoes change during strain.

The characteristic features of elastic properties and behavior of polyurethane during strain, the expressed in capability for auto/self-curing defects during the development of cracks and high resistivity to voltage/stresses, in many respects they are determined by the type of three-dimensional/space grid. It differs from the common vulcanization the fact that the contribution of physical reactions to effective network density is extremely great. Possibility of redistributing the molecular bonds in polyurethane rubbers during strain - one of the reasons for manifestation by these polymers of special properties.

Therefore it is interesting to investigate the thermodynamics of the highly elastic strain of polyurethane elastomers and to establish/install the contribution of inner energy and entropy to the elastic force, which appears during the strain of elastomer. In this direction are known only several works [69, 72, 75, 117, 192, 325, 326, 328], carried out, in essence, in recent years.

As is known, the calculations of entropy and energy components of the equilibrium voltage/stress, applied to the specimen/sample of rubber with its stretching, are conducted through the straight lines of the dependence of equilibrium voltage/stress from the temperature

during different elongation, called thermo-elastic. In this case, is used the common/general/total equation of kinetic theory of rubber elasticity [137, 211]

$$f = f_U + f_S = \left(\frac{dU}{dl} \right)_{T,V} - T \left(\frac{dS}{dl} \right)_{T,V} = \left(\frac{dU}{dl} \right)_{T,V} + \\ + T \left(\frac{df}{dT} \right)_{V,l} \approx \left(\frac{dU}{dl} \right)_{T,V} + T \left(\frac{df}{dT} \right)_{P,\lambda},$$

where U - inner energy; S - entropy; l - length of specimen/sample; f - tensile force; f_U - elastic component of equilibrium force; f_S - entropy component of equilibrium force.

Changes in the inner energy of rubbers usually are very insignificant and if they are developed, then with the high amounts of strain.

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Conway [192], investigating the contribution of energy and entropy components of polyurethane rubber on the basis of polyoxypropyleneglycol, also noted an insignificant change in the inner energy during slight deformations. However, in all further works [69, 72, 75, 117, 325, 326, 328], which concern thermodynamics it is polyurethane, it is indicated significant changes in the inner energy even during slight deformations. So, Tanaka and coworkers

[326], studying the dependence of voltage/stress from the temperature it is polyurethane on the basis of complex and simple polyether/polyesters in the range of temperatures of 40-70°C, they showed that during strain it occurs both the decrease and an increase in the inner energy it is polyurethane depending on the nature of the latter. The dependence of the contribution of energy component into common/general/total equilibrium voltage/stress f_{v} from the degree of stretch of elastomers is changed in absolute value and on sign with an increase in the degree of stretch and a change in the nature of components is polyurethane (Fig. 100). In essence is observed the decrease of energy component of equilibrium voltage/stress. The obtained results are explained by a change in the chain conformations during the strain of elastomers. For polyurethane on the basis of naphthylenediisocyanate (curve 2) abrupt change f_{v} with the degree of stretch is explained by crystallization; however, there are no experimental proofs.

Is investigated the thermodynamics of the highly elastic deformation of linear ones it is polyurethane, developing highly elastic properties in an interval temperatures of 20-70°C at large stretchings [289], and obtained the dependence of equilibrium voltage/stress and its components with the degree of stretching for some it is polyurethane [325] (Fig. 101).

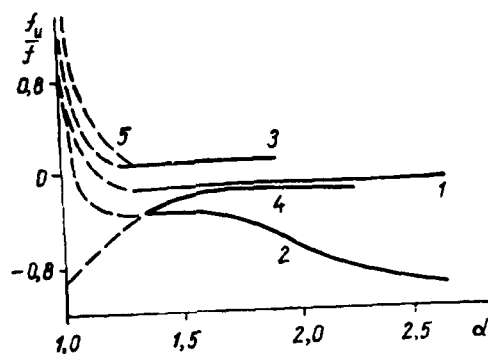


Fig. 100. Dependence of f_u/f on the quantity of deformation of polyurethane elastomers (4):
 1 - based on TDI and TMP polyethylene glycol adipate; 2 - based on polyethylene glycol adipate, naphthylene diisocyanate, and butane-diol; 3 - based on TDI and TMP polypropylene glycol adipate; 4 - based on TDI polyethylene glycol adipate and ethanol amine; 5 - based on TDI polypropylene glycol and ethanol amine.

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Table 57. The composition of studied polyurethanes.

(1) Образец	(2) Полиэфир	(3) Изоцианат	(4) Сшивающий агент	(5) Мольное соотношение	M_c
1	(6) ПДЭГА (мол. вес 1600)	2,4-ТДИ	(7) Полиол (6) FIV	—	15 400
2	То же (8)	То же (8)	ДЭА + ТЭА (1:1,5)	1.0:1.2:0.1	11 800
3	" "	" "	То же (8)	1.0:1.3:0.13	11 500
4	" "	" "	" "	1.0:1.4:0.20	10 200
5	(6) ПДЭГА (мол. вес 800)	2,4-ТДИ + ГМДИ (20:80)	Полиол * (7)	1.0:1.4:0.20	6000
6	(6) ПДЭГА (мол. вес 1600)	То же (8)	(9) Глицерин + ДЭГ (3:1)	1.0:1.4:0.20	2900
7 (10)	Разветвленный ДЭГА	2,4-ТДИ	—	1.0:0.85	4500
8	(6) ПДЭГА (мол. вес 900)	2,4-ТДИ	(9) Глицерин + ДЭГ (1:1)	—	2250
9	То же (8)	То же (8)	(9) Глицерин + ДЭГ (3:1)	—	4200
10	(6) ПДЭГА (мол. вес 1750)	" "	То же (8)	—	4200
11	(6) ПДЭГА (мол. вес 900)	" "	(9) Глицерин + ДЭГ (1:1)	—	6200
12	(6) ПДЭГА (мол. вес 900)	2,4-ТДИ	(9) Глицерин + ДЭГ (3:1)	—	2600

TABLE 57. (CONTINUED)

13	ПЭГА (мол. вес 1000)	То же ⑧	Глицерин + ДЭГ (1:1)	—	6600
14	То же ⑧	» »	Глицерин + ДЭГ (3:1)	—	4400
15	ПЭГА (мол. вес 2000)	» »	Глицерин + ДЭГ (1:1)	—	23 800
16	То же ⑧	» »	Глицерин + ДЭГ (3:1)	—	7700
17**	» »	» »	Глицерин + ДЭГ (1:1)	—	—
18**	» »	» »	Глицерин + ДЭГ (3:1)	—	—
19	ПТМД (мол. вес 1000)	» »	ТМП	1:2:1	5100
20	То же ⑧	ДМДИ	То же ⑧	1:2:1	4300
21	ПТМД (мол. вес 1540)	2,4 - ТДИ	1,4-Бутандиол + ТМП	1:2:1	1900
22	ПТМД (мол. вес 960)	То же ⑧	Глицерин + ДЭГ (1:1)	—	10 060
23	То же ⑧	» »	Глицерин + ДЭГ (3:1)	—	3350
24	ПОПД (мол. вес 1010)	» »	Глицерин + ДЭГ (1:3)	—	13 000
25	ПОПД (мол. вес 2050)	» »	То же ⑧	—	18 300

Key: (1). Specimen/sample. (2). Polyether/polyester. (3). Isocyanate. (4). Crosslinking agent. (5). Molar ratio. (6). PDEGA (mol. weight 1600). (7). Polyol ¹.

FOOTNOTE ¹. Polyol on the basis of adipic acid, glycerin and diethylene glycol. ENDFOOTNOTE.

(8). The same. (9). Glycerin. (10). 1,4-Butanediol.

FOOTNOTE ². M_c they did not determine due to the crystallization of specimen/samples.

Page 180. In this case it is observed both increase in the inner energy with the stretching of the investigated specimen/samples (Fig. 101b) and decrease (Fig. 101a). Last/latter fact is bonded with crystallization during the deformation, confirmed by X-ray method. With the stretching of polyurethane on the basis of polycarbonatediol when occurs increase of inner energy during deformation, crystallization was not noticed even with stretching to 500o/o.

We studied the thermodynamics of the highly elastic deformation of polyurethane elastomers on the basis of simple and polyesters [69, 72, 75, 117]. As polyesters are undertaken linear and branched polydiethyleneglycoladipate (PDEGA) and polyethyleneglycoladipate

(PEGA), as simple ones - polyoxitetramethylenediol (PTMD) and polyoxypropylenediol (PCPD); are used such diisocyanates, as mixture 2,4- and 2,6-TDTs (T-102), hexamethylene diisocyanate (G-102), diphenylmethane diisocyanate (DMI). The crosslinking agents were trimethylol propane (TMP), mixture of 1,4-butanediol with TMP, polyol on the basis of adipic acid, diethylene glycol and glycerin, mixture of triethanolamine and diethanolamine (TEA+DEA). The characteristics of the investigated specimen/samples, and also the value of average molecular weights between network points (M_c), calculated by the value of the equilibrium modulus of high elasticity, are given in Table 57.

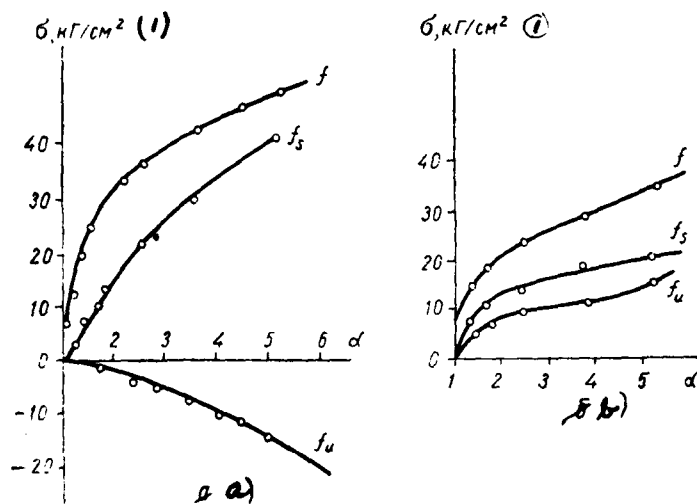


Fig. 101. Change in equilibrium voltage/stress and its components from degree of stretching for is polyurethane on of polycaprolactone diol and m-xylylenediamine (a); polycarbonate diol and

ethylenediamine (b).

Key: (1) . kg/cm².

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The dependence of stress level from temperature was measured on a relaxometer designed according to type [27]. For maintaining the constancy of relative elongation in the course of measurements, it was necessary to know a change in the lengths of the unstressed specimen/sample with temperature which render/showed insignificant. Therefore subsequently during great lengthenings these changes they disregarded, but during small extracts (to 100/o) in the calculations of the values of the equilibrium voltage/stress were considered changes in the length of the unstressed specimen/sample with temperature. Energy and entropy components calculated from thermo-elastic straight lines (dependence of equilibrium voltage/stress from temperature), using equation (VII, 1). From the dependence of equilibrium voltage/stress and its components from temperature (Fig. 102) and degree of elongation (Fig. 103) it is evident that with stretching it is polyurethane, as for common rubbers, is observed the decrease of entropy, bonded with the decrease of a number of chain conformations during extract. But in contrast to the majority of rubbers where a change in the inner

energy during extract is close to zero (with stretching to 1000/o) [137], for is polyurethane different nature relative elongation 8-100/o already it causes the sharp decrease of inner energy in all cases. The decrease of the inner energy of the natural rubber occurs during the extract of higher than 3000/o, which is explained by crystallization [137].

The roentgenographic measurements of the deformed polyurethane specimen/samples did not reveal/detect crystallization in the range of deformations from 0 the 1000/o (Fig. 104, see insert). Therefore, the observed decrease of inner energy during deformation to 1000/o it is not bonded with crystallization, as is assumed [325, 328].

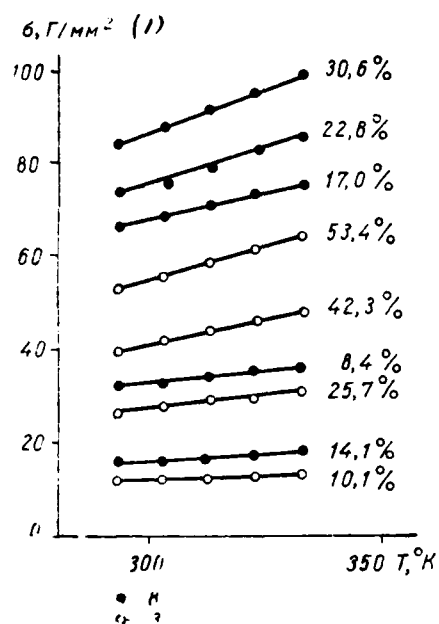


Fig. 102. Dependence of equilibrium voltage/stress (σ) from temperature for specimen/samples 8 and 13. (designations see in Table 57).

Key: (1). Г/мм^2 .

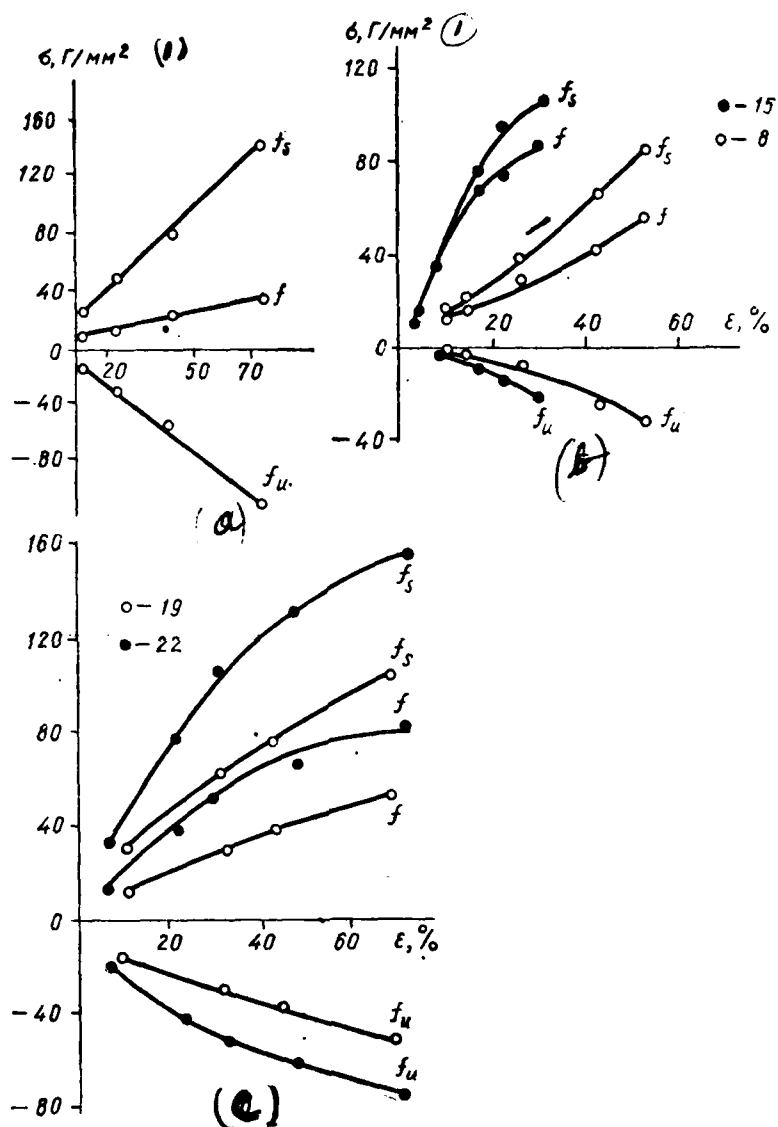


Fig. 103. The dependence of equilibrium voltage/stress and its components from the amount of deformation (a) for specimen/samples 1 (a), 8 and 13 (b), 19 and 22 (c) (designations see in Table 57).

Key: (1) . G/mm².

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For the explanation of the observed decrease of inner energy with stretching, it is polyurethane one should consider that the fact that in the latter together with chemical ones is a large number of physical bonds, which contribute the significant contribution to common/general/total density of the three-dimensional grid. Really/actually, earlier we examined a question concerning the nature of molecular bonds and established that the diversity of functional groups in chains determines the existence of the collection of the bonds, which differ in strength from common van der Waals ones to hydrogen ones. At different temperatures and with voltage/stresses, occurs the decomposition of these bonds, which as a result of their diversity can occur/flow/last in the wide temperature range and be gradual. This lability of these bonds, and also different effect of external voltage at this temperature on the change of the strength of bond play the significant role in the thermodynamic properties of these elastomers. The special feature/peculiarities indicated determine the lightness/ease of the rearrangement of three-dimensional grid it is polyurethane during the deformation of

the latter. Tensile strain contributes to the approach of the cuts of the chains between nodes, which causes the formation of the additional physical bonds between them and thereby the decrease of inner energy which is observed in the case amorphous polyurethane elastomers even with the small degrees of stretching.

It is obvious, an increase in the flexibility of the cuts of the chains between nodes as a result of an increase in molecular weight of oligoester block or M_c because of a smaller quantity of the crosslinking agent will increase the possibility of the formation of physical bonds during deformation as a result of the approach of the cuts of chains with each other. The dependence of the contribution of energy component into the common/general/total voltage/stress from the degree of the stretching of polyurethane on the basis of polyethyleneglycoladipate of different molecular weights confirms this assumption (Fig. 105).

From dependence f_u/f on value M_c for it is polyurethane on the basis of complex and polyethers (Fig. 106) it is evident that f_u/f correlates with M_c . During decrease M_c , i.e. during an increase in the network density, the degree of a change in the inner energy becomes less.

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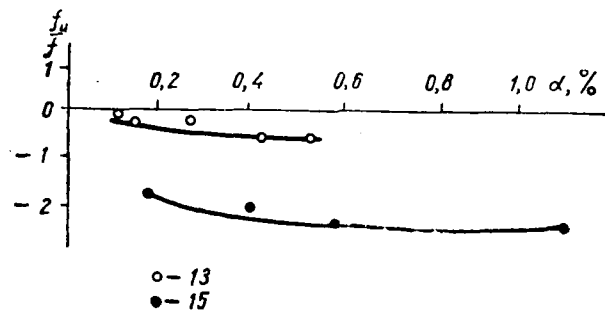


FIG. 105.

Fig. 105. Dependence of the contribution of energy component into equilibrium voltage/stress from value deformation.

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Probably, during the deformation of the strongly cross-linked elastomers as a result of the greater hardness of the cuts of the chains between nodes, decreases the possibility of shaping of additional physical bonds.

For it is polyurethane on the basis of polyesters change $[v']$ it is more noticeably than in polyurethane on the basis polyethers. The reason for the observed phenomenon consists in a difference in the portion/fraction of chemical and physical cross-linkings in the common/general/total network density of these elastomers. If in polyurethane on the basis of polyesters the dominant role in grid belongs to physical bonds, then in elastomers on the basis polyethers the contribution of physical bonds will be less.

The analysis of Fig. 106b shows that a change of the inner energy in polyurethane on the basis of oligoethylene- and oligodiethyleneglycoladipate is approximately equal, in spite of different values M_c . Probably, the great flexibility of the cuts of

chains in polyurethane on the basis of oligodiethyleneglycoladipate contributes to the formation of a large number of molecular bonds in the course of tensile strain even when smaller M_c than in it is polyurethane on the basis of oligoethyleneglycoladipate. This causes a greater change of the inner energy in the first case, than the secondly despite the fact that M_c polyurethane on the basis of oligodiethyleneglycoladipate is less.

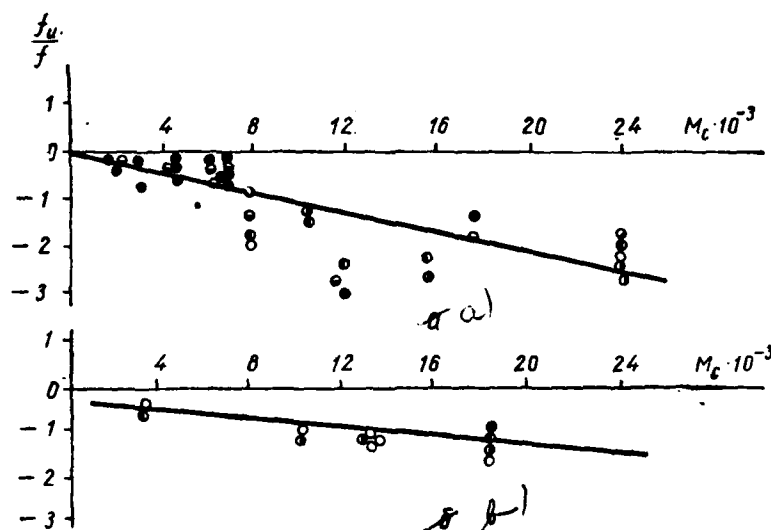


Fig. 106. Dependence f_u/f on M_c for amorphous it is polyurethane on basis of complex (a) and simple (b) polyether/polyesters with stretching from 10 to 60o/o.

Some of those investigated by us it is polyurethane they were spontaneously crystallized in the course of time [75]. Was studied the thermodynamics of the deformation of these specimen/samples (Fig. 107), which is accompanied by an increase in both entropy and inner energy. It is possible to count that in this case occurs the destruction of crystalline formations, i.e., the decrease of degree of order, which leads to an increase in the entropy. In this case, logical to expect the increase in the inner energy that usually occurs during the deformation of crystalline bodies.

Thus, findings tell about the fact that a change in the inner energy during the deformation of polyurethane elastomers depends both on nature and network density of polyurethane and on the phase state of the latter.

It is obvious, the deformation of the elastomers indicated in the range of higher temperatures will lead to a change in the thermodynamic functions, since it is known that the physical bonds whose concentration is great in polyurethane, it is very sensitive to temperature effects. Therefore we investigate the thermodynamics of the deformation of polyurethane amorphous elastomers in the range of temperatures of 100-60°C [117] and will compare the character of a change of the thermodynamic functions in this case with the same in the range of lower temperatures (20-60°C).

Preliminarily was conducted the isometric heating of the specimen/samples being investigated with different loads for the establishment of the temperature range, in which does not occur the decomposition of the grid of chemical bonds, as a result of which were obtained the curves of the isometric heating of polyurethane elastomers (Fig. 108). Initially occurs the increase in the voltage/stresses in specimen/samples, caused by the effort/force of the thermal agitation of chains with an increase in the temperature. With an increase in the original load on specimen/sample, a change in the voltage/stress in polyurethane with a temperature rise becomes more noticeable. Then in the range of temperatures of 100-120°C (depending on load on specimen/sample) begins a sharp voltage drop.

It is known that polyurethane are characterized by the presence of the chemical bonds of different types. It is assumed that biuret and allophanate bonds least strong/durable [302].

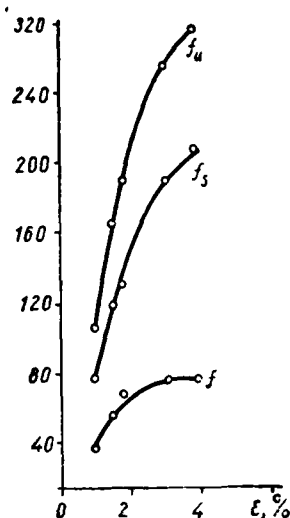


Fig. 107. The dependence of the equilibrium voltage/stress f and of its components f_u and f_s from the degree of elongation for specimen/sample 18 (designation see in Table 57).

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There are data about the fact that at temperatures of 106°C or above begins the dissociation of the allophanate bonds [249]. It is possible, this causes a sharp voltage drop at temperatures in higher than 100°C. For the confirmation of the fact that in this case occurs the decomposition of chemical bonds, is investigated the reversibility isometric heating (Fig. 109). On the isometric curves is observed hysteresis. In the temperature range of 20-100°C, value

of hysteresis is insignificant. Large hysteresis in interval of 20-130°C testifies to the irreversibility of deformation, bonded with the irreversible decomposition of the grid of chemical bonds. Consequently, the thermodynamics of deformation can be traced only to 100°C, i.e., to the temperature, at which yet does not disintegrate the chemical grid of bonds.

The analysis of thermo-elastic straight lines for polyurethane on the basis of polyester (Fig. 110) and of dependence of the equilibrium voltage/stress π and of its components from the degree of elongation (Fig. 111) shows that during the deformation of polyurethane elastomers occurs the decrease of both entropy and inner energy.

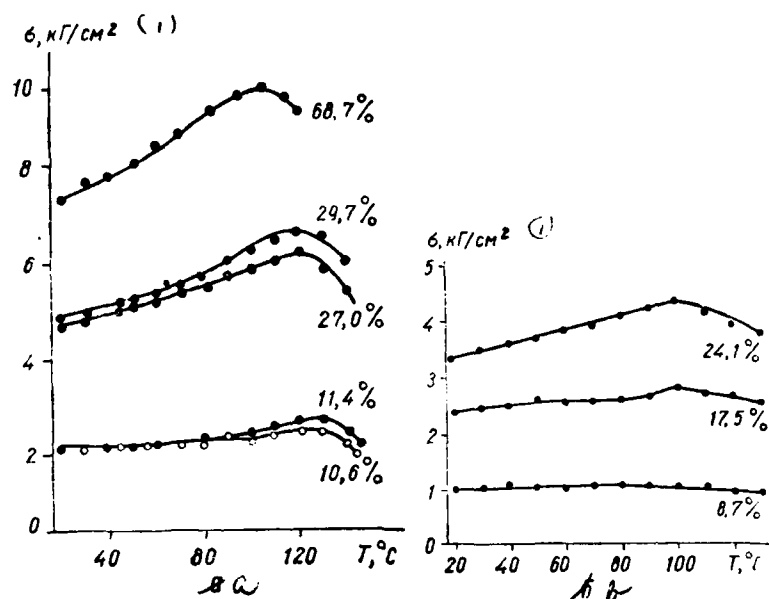


Fig. 108. The curves of isometric heating for it is polyurethane: a - on the basis of PEGA (specimen/sample 13, table 57); b - on the basis of PDEGA (specimen/sample 10).

Key: (1) . kgf/cm^2 .

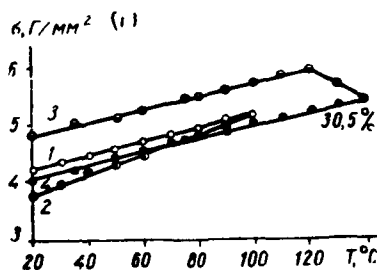


Fig. 109. Curves of isometric heating for specimen/sample 1 (table

57) in different temperature ranges: 1, 2 - lift and decrease in temperature in interval of 20-100°C; 3, 4 - lift and decrease in temperature in interval of 20-130°C.

Key: (1). G/mm².

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On the other hand, thermo-elastic straight lines in the range of temperatures of 100-60°C lie/rest below than at 60-20°C. It is obvious, heating specimen/sample to 100°C leads to the dissociation of the greater part of the physical bonds. Otherwise, we deal with the three-dimensional/space grid, which possesses the smaller concentration of physical bonds, which leads to the decrease of the effective density of cross-linking and, therefore, to an increase in the effective flexibility of the chains between chemical network points.

We note that during the deformation of polyurethane elastomers with the less density of cross-linking a change in the inner energy during deformation is considerably more than in the case of elastomers with the high density of cross-linking. It is analogous, the deformation of elastomers at high temperatures is accompanied by a large change in the inner energy, than at low temperatures (Fig. 111, 112a).

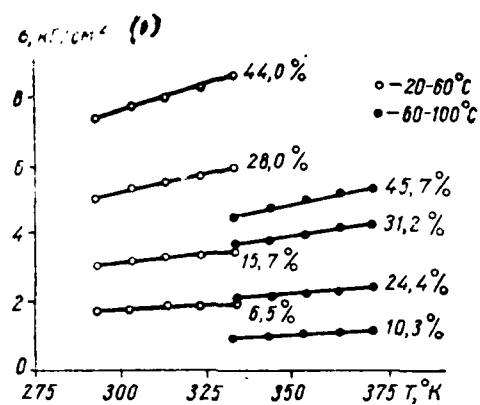


Fig. 110. Thermo-elastic straight lines for specimen/sample 14 (table 57) in different temperature intervals.

Key: (1) . kgf/cm^2 .

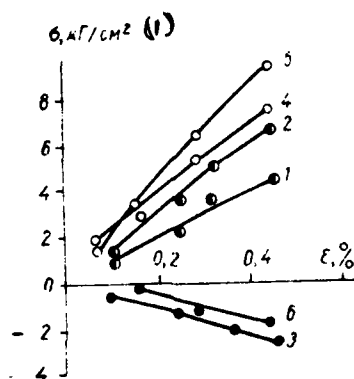


Fig. 111. Dependence of equilibrium voltage/stress and its components

from amount of deformation (specimen/sample 14, table 57):

1, 2, 3 - f_u and Δ in region 80 - 100 °C; 4, 5, 6 - f_u

and f_u in region of 20-60°C.

Key: (1). kgf/cm².

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This is explained by the fact that with the drawing of specimen/sample in the high-temperature range when the part of physical bonds is destroyed and the cuts between nodes possess greater flexibility, is created the great possibility of reducing the old ones and the formations of new physical bonds during the approach of the cuts of chains, while energy component of equilibrium voltage/stress grow/increases.

During the deformation of polyurethane elastomers on the basis polyethers at elevated temperatures, a change in the inner energy is also more than in the range of low temperatures (Fig. 112a, b). The sharper difference between values f_u/f in different temperature intervals during the deformation of polyurethane with the less

effective density of cross-linking (Fig. 112b, c) is logical in light of consideration about a change in the flexibility of the cuts of chains at the different densities of the cross-linking of three-dimensional grid.

It is known that the measurement of the dependence of the equilibrium voltage/stress on the elongated polymeric specimen/sample from temperature is the basis of the method of calculation of the temperature coefficient of the size/dimensions of free polymer chain in undisturbed state [212-214]. Method is based on the theory of the elasticity of rubbers, which assumes the independence of intermolecular interaction from deformation, and on the principle of additivity [215] of the contributions of free energy of separate chains to common/general/total free energy of system. Calculations are based on the equation

$$f_U/fT = -[d \ln(f/T)/dT]_{V,L} = d \ln \bar{r}_0^2/dT.$$

If measurements voltage/stress - temperature are conducted at a constant pressure, this equation is record/written in the form

$$[-d \ln(f/T) dT]_{P,L} = d \ln \bar{r}_0^2/dT + \frac{3\beta}{\lambda^3 - 1}, \quad (\text{VII}, 2)$$

where $d \ln \bar{r}_0^2/dT$ - temperature coefficient of the root-mean-square distance between the ends of chain; β - cubic coefficient of the expansion of elastomer; λ - degree of stretch of elastomer.

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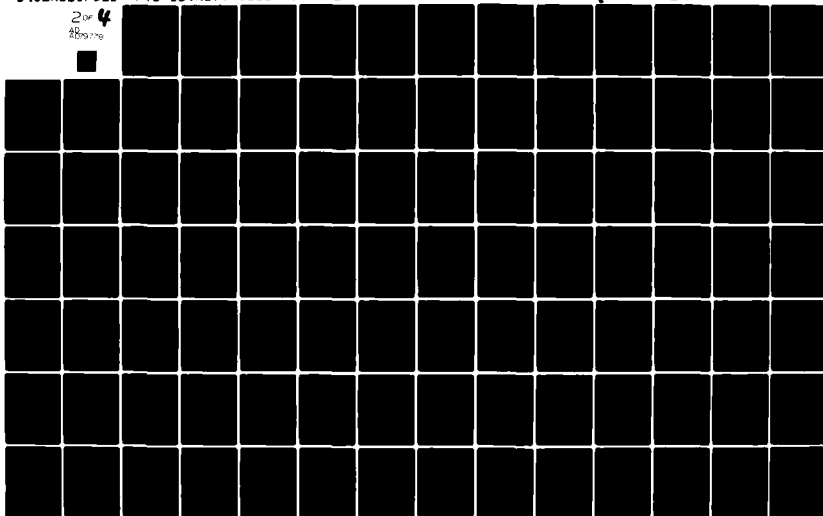
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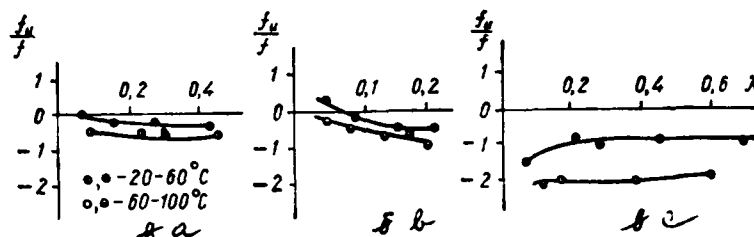


Fig. 112. Dependence f_u/f on the degree of stretch λ for it is polyurethane on the basis of complex (a) and simple polyether/polyesters (b, c): a - specimen/sample 14; b - specimen/sample 23; c - specimen/sample 22 (designations see in Table 57).

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Processing/treatment [69] of the obtained by equation (VII.2) data will show (table 58) that the values of value f_u/fT were negative in all cases, which indicates the decrease of sizes of the undisturbed polymer chain to temperature. Together with value f_u/fT strongly they are distinguished by absolute value, which would seem completely natural, if we consider different composition of those investigated was polyurethane. But these differences are retained also in the case of one and the same by the qualitative composition of polyurethane (specimen/samples 14, 15) with the different degree

of cross-linking. Dependence f_0/T on the degree of cross-linking is observed even when the objects of study will be polyethylene, polypropylene and their copolymers [284].

The method of calculation of the temperature coefficient of the size/dimensions of free polymer chain is based on the assumption that a change in the inner energy during the deformation of elastomer is caused by a change only in intramolecular reaction; a change in intermolecular interaction is not considered. Meanwhile it cannot be assumed that the significant change in the inner energy, observed with stretching it is polyurethane, it is caused by an increase in the intramolecular reaction, since the drawing of the cuts of polymer chains contributes to the removal of polar groups in chain from each other and is decreased the probability of their intramolecular reaction. Probably, in the process of extract, it is polyurethane it occurs the approach of the cuts of the chains between nodes, which leads to the formation of additional physical nodes in grid due to the reaction of the polar groups of adjacent chains. Thus, the decrease of inner energy during the extract of polyurethane elastomers is caused, in the first place, by a change in intermolecular interaction of the cuts of polymer chains. The change in the inner energy the greater, the greater the distance between nodes in grid.

In connection with that presented for it is polyurethane it is not possible to obtain the plausible values of changes in the root-mean-square distance between the ends of free chain from given voltage/stress - temperature.

The conducted investigations show that the presence in polyurethane of the physical bonds of different types leads to another behavior under the deformations and the temperature influences of this class of rubbers in comparison with natural and other rubbers [72, 325, 326, 328]. The given special feature/peculiarities are bonded with the presence of movable grid of physical bonds and with its rearrangement in the course of the deformation and temperature effects, by which appears the new structure, which corresponds to state of strain. When the rates of deformation and rearrangement of grid will be compared, is establish/installed new equilibrium in system, which is very important in the examination of the mechanism of the deformation of polyurethane elastomers.

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Table 58. Equilibrium voltage/stresses and their components of polyurethanes of different degree of cross-linking.

(1) Образец		$f, \text{ кг/см}^2$	$\frac{1}{T} \left(\frac{df}{dT} \right)_{V,T}$	$\frac{1}{U} \left(\frac{dU}{dT} \right)_{V,T}$	U/RT	M_c
1	1.12	1.01	-2.40	-1.39	-1.37	15 400
	1.24	1.53	-4.78	-3.25	-2.12	
	1.44	2.26	-7.17	-4.91	-2.17	
	1.76	3.62	-14.14	-10.52	-2.9	
2	1.19	0.97	-4.52	-3.55	-2.94	11 800
	1.53	2.83	-6.79	-3.96	-1.39	
	*1.80	3.80	-9.21	-5.41	-1.42	
	2.00	4.13	-13.50	-9.37	-2.27	
3	1.13	1.16	-4.30	-3.14	-2.70	11 500
	1.20	1.36	-5.24	-3.88	-2.85	
	1.32	2.17	-8.33	-6.16	-2.84	
	1.84	3.37	-13.55	-7.02	-2.90	
4	1.29	2.90	-7.20	-4.3	-1.48	10 200
	1.35	3.51	-8.00	-4.49	-1.28	
	1.45	4.90	-10.70	-5.80	-1.18	
	1.60	5.30	-13.70	-8.40	-1.58	
5	1.03	1.19	-1.59	-0.40	-0.34	6000
	1.08	2.30	-2.87	-0.57	-0.25	
	1.13	3.37	-4.12	-0.75	-0.22	
	1.17	4.25	-5.34	-1.09	-0.26	
6	1.33	8.98	-11.17	-2.19	-0.24	2900
	1.04	1.31	-2.34	-1.03	-0.78	
	1.06	2.28	-4.36	-2.08	-0.91	
	1.07	3.18	-5.96	-2.78	-0.87	
7	1.13	4.50	-8.24	-3.74	-0.83	4500
	1.07	1.30	-1.70	-0.40	-0.30	
	1.09	1.55	-2.43	-0.88	-0.57	
	1.11	2.10	-3.40	-1.30	-0.62	
8	1.24	2.98	-4.66	-1.68	-0.56	2250
	1.04	1.60	-1.41	0.19	-0.12	
	1.08	3.30	-3.53	-0.23	-0.07	
	1.17	6.85	-7.52	-0.67	-0.10	
9	1.23	7.60	-9.32	-1.72	-0.23	4200
	1.31	8.76	-10.75	-1.99	-0.23	
	1.06	1.10	-1.25	-0.15	-0.14	
	1.09	1.90	-2.80	-0.90	-0.50	
10	1.21	4.60	-6.30	-1.70	-0.37	4200
	1.26	4.85	-6.62	-1.77	-0.37	
	1.33	5.40	-8.14	-2.74	-0.50	
	1.06	1.10	-1.25	-0.15	-0.14	
	1.09	1.90	-2.80	-0.90	-0.50	
	1.21	4.60	-6.30	-1.70	-0.37	
	1.26	4.85	-6.62	-1.77	-0.37	
	1.33	5.40	-8.14	-2.74	-0.5	

Key: (1). Specimen/sample. (2). kgf/cm².

Continuation Table 58.

(1) Образец	λ	(2) $I, \text{ кг/см}^2$	$\frac{d}{dt} \left(\frac{I}{V, T} \right)$	$\frac{dU}{dt} \left(\frac{V, T}{I} \right)$	I_U/IT	M_c
11	1.03	0.78	0	0.78	1.0	6200
	1.08	1.70	-2.51	-0.81	-0.48	
	1.15	2.90	-4.10	-1.20	-0.41	
	1.21	4.50	-7.75	-3.25	-0.72	
	1.35	6.15	-10.18	-4.03	-0.66	
12	1.02	1.18	-1.35	-0.15	-0.13	2600
	1.06	2.70	-3.19	-0.49	-0.18	
	1.13	4.50	-5.50	-1.00	-0.22	
13	1.10	1.25	-1.44	-0.19	-0.15	6600
	1.14	1.70	-2.12	-0.42	-0.25	
	1.26	2.88	-3.62	-0.79	-0.28	
	1.42	4.25	-6.74	-2.49	-0.59	
	1.52	5.60	-8.61	-3.01	-0.54	
14	1.06	1.80	-1.66	0.15	0.08	4400
	1.16	3.10	-3.22	0.12	-0.04	
	1.28	5.25	-6.47	-1.22	-0.23	
	1.44	7.56	-9.31	-1.75	-0.23	
15	1.16	0.40	-1.12	-0.72	-1.80	23 800
	1.39	0.90	-2.78	-1.88	-2.10	
	1.58	1.20	-4.18	-2.98	-2.48	
	2.09	1.60	-5.63	-4.03	-2.52	
16	1.10	0.65	-1.16	-0.51	-0.8	7700
	1.25	1.68	-4.63	-2.5	-1.7	
	1.49	2.85	-8.46	-5.61	-1.9	
17	1.008	3.06	17.49	20.55	6.71	Кристал- лический (3)
	1.009	4.80	19.92	24.72	5.15	
	1.020	6.40	21.80	28.20	4.41	
18	1.010	2.95	6.87	9.72	3.29	Кристал- лический (3)
	1.015	4.70	11.00	15.70	3.34	
	1.018	5.93	12.31	18.84	3.07	
	1.031	6.62	18.23	24.85	3.75	
	1.039	6.65	20.55	27.20	4.09	
19	1.11	1.36	-3.05	-1.69	-1.24	5100
	1.32	2.98	-6.18	-3.20	-1.07	
	1.43	3.78	-7.57	-3.79	-1.00	
	1.67	5.27	-10.50	-5.23	-0.99	
20	1.04	0.96	-2.54	-1.58	-1.64	4300
	1.10	2.17	-4.78	-2.61	-1.20	
	1.15	3.31	-7.33	-4.02	-1.21	
	1.69	8.25	-15.34	-7.09	-0.86	
21	1.05	2.48	-3.73	-1.25	-0.50	1900
	1.10	4.48	-6.28	-1.80	-0.40	
	1.17	6.69	-8.66	-1.97	-0.29	

Key: (1). Specimen/sample. (2). kg/cm^2 . (3). Crystalline.

Continuation Table 58.

(1) Образец	λ	(2) $f, \text{кг/см}^2$	$\left(\frac{dS}{d\lambda}\right)_{v,T}$	$\left(\frac{dU}{d\lambda}\right)_{v,T}$	f_U/f_T	M_c
22	1.07	1.23	-3.2	-1.98	-1.60	10 060
	1.22	3.85	-7.24	-3.39	-0.88	
	1.30	5.30	-11.15	-5.85	-1.10	
	1.47	6.00	-13.07	-6.33	-0.96	
	1.71	8.20	-15.82	-7.62	-0.93	
23	1.04	1.85	-1.36	0.49	0.26	13 000
	1.09	3.55	-4.56	-1.01	-0.28	
	1.16	6.50	-9.56	-3.06	-0.47	
	1.21	9.80	-14.70	-4.80	-0.49	
24	1.20	1.35	-2.90	-1.55	-1.15	18 300
	1.22	1.82	-3.67	-1.86	-1.02	
	1.30	2.55	-5.64	-3.09	-1.21	
	1.38	3.60	-8.08	-4.48	-1.24	
25	1.14	0.65	-1.29	-0.64	-0.92	18 300
	1.33	1.30	-2.96	-1.66	-1.30	
	1.39	1.65	-3.90	-2.25	-1.40	

Key: (1). Specimen/sample. (2). кг/см^2 .

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Really/actually, in the presence of movable grid at each stage of deformation, is necessary further decomposition of grid in contrast to other elastomers where the deformation is not accompanied by the reduction of the initially destroyed bonds. We assume that the comparative lightness/ease of decomposition and reduction of grid explains the capability it is polyurethane for the curing of defects

during deformation, which can be considered as a thixotropic change in the three-dimensional/space grid.

THERMAL EFFECTS DURING DEFORMATION OF POLYURETHANES.

It is known that the mechanical deformation of polymers is invariably accompanied by the thermal effects whose sign depends on the form of deformation, phase and physical states of the polymer being deformed.

Studies of the thermal effects of deformation is of essential interest, since it gives important information about thermodynamics and to the molecular nature of this process. However, works in this direction it is small, which is caused by the difficulties of the quantitative determination of the thermal effects, which accompany deformation, because their values are very insignificant. The first essential works in this direction they are made by Mueller/Muller and coworkers [99, 275], who developed the gas-filled differential microcalorimeter.

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We carried out the determination of the thermal effects, which accompany the deformation of polyurethane elastomers [47, 75], on the

special block, which makes it possible to simultaneously record/write differential temperature slope and change in the voltage/stress with deformation and relaxation of specimen/sample. As the subjects of investigation serve polyurethane on the basis of 2,4-DTI and polyethyleneglycoladipate (PEGA) of different molecular weight (Table 59).

PEGA easily is crystallized, which can lead to crystallization and is polyurethane on their basis. However, as it is noted in [15], spontaneous crystallization was polyurethane, containing the crystallizing oligoester blocks, it occur/flow/lasts only at the sufficient length of the oligoester blocks when the rigid diisocyanate blocks of macro-chain no longer can interfere crystallization.

Really/actually, even after semiannual aging at room temperature spontaneous crystallization is observed only for specimen/sample by 3 (see Table 57). Specimen/sample 3 (see Table 57). To this, testifies the character of thermograms [42, 75].

The character of the thermal effects of the deformation of specimen/sample 1 (Fig. 113) is analogous such for the highly elastic deformation of other polymeric systems, i.e., the stretching of specimen/sample is accompanied by heat liberation. This is explained

by the decrease of the entropy of system, which occurs as a result of the decrease of a number of conformations of macromolecules in polymer in the course of the process. Relieving stress and abbreviation in the specimen/sample is accompanied by heat absorption. Consequently, the investigated polyurethane during deformation develops the properties of an entropy-elastic material.

Figure 114 gives the quantitative dependence of the areas of the peaks of the thermal effects of stretching on the temperature in two successive deformation cycles for specimen/samples 1 and 2.

During the repeated cycle of tensile strain, of both of specimen/samples is accompanied by large exothermic effect than with primary stretching; grow/increase the values of thermal effects, also, with a temperature rise.

Table 59. The characteristic of those investigated it is polyurethane.

(1) Образец	(2) Полиэфир	(3) Сплавляющий агент (ДЭГ + + глицерин)	M_c
1	ПЭГА-1000	1:3	3800
2	ПЭГА-1000	1:1	5400
3	ПЭГА-2000	1:1	23 800

Key: (1). Specimen/sample. (2). Polyether/polyester. (3).

Crosslinking agent (DEG + glycerine).

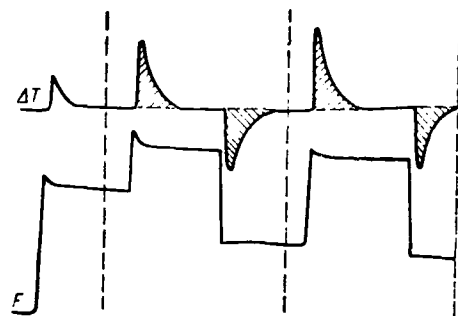


Fig. 113. Thermogram of stretching and abbreviation in specimen/sample 1 (Table 57).

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For it is polyurethane with a significant quantity of physical bonds of a difference in the thermal effects during repeated cycles or with an increase in the temperature it is possible to explain by the fact that after the primary process of the decomposition of bonds, accompanied by heat absorption, in the second cycle predominate only entropy changes. The same takes place, if the part of the physical bonds disintegrates with an increase in the temperature.

Since in our case deformation thermodynamically unbalanced, is observed certain difference in the thermal effects of stretching and abbreviation.

The character of the thermograms of specimen/samples 1 and 2 is analogous; however, due to the less density of chemical cross-linking, last/latter specimen/sample more is elastic, which conditions the larger values of thermal effects and the smaller values of the voltage/stress of specimen/sample with the identical

degrees of deformation.

Even the semiannual aging of specimen/samples 1 and 2 at room temperature does not lead to a change in the original character of thermal effects with their deformation.

Moreover the character of thermal effects during the deformation of specimen/sample 3 depends substantially on the duration of its aging, which undoubtedly is caused by development in polyurethane in the course of time of crystal structure of different degree of perfection. In the initial stage (immediately after obtaining or heating with 50°C) the character of the thermal effects of the deformation of specimen/samples 1, 2 and 3 is identical, i.e., polyurethane behaves as entropic-elastic material.

However, after semimonthly aging the character of the thermal effects of the deformation of specimen/sample 3 substantially is changed (Fig. 115).

In contrast to specimen/sample 1 stretching of specimen/sample 3 is accompanied heat absorption. This phenomenon can be bonded with the simultaneous course the elastic deformation, occurring in the initial stage of stretching and caused by the presence in the specimen/sample of 3 crystalline phases, and the decomposition of

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crystalline phase, which can occur/flow/last with stretching and it is also accompanied by heat absorption.

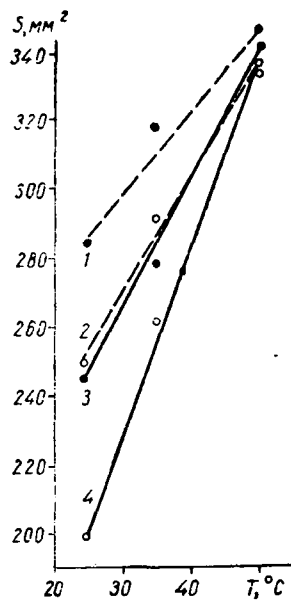


Fig. 114. The temperature dependence of the areas of the exothermic peaks of the stretching of specimen/samples 1 (curves 1, 3) and 2 (curves 2, 4). Solid lines - I cycle of stretching, broken - II cycle of the stretching (designations see in Table 57).

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In this case, in contrast to specimen/samples 1 and 2 after the rapid stretching of specimen/sample 3, is observed stress relaxation, which is accompanied by heat liberation, about which tells wide exothermic maximum on differential in temperature slope. This indicates that together with the described processes in the course of

stretching is developed, in proportion to an increase in the content of amorphous phase, the common process of highly elastic deformation, whose heat is first completely compensated for by heat the indicated above two processes, which are prevailing in the initial stage of deformation.

However, the decomposition of crystalline phase stops in the course of time, and the development of highly elastic deformation is continued, that also is reflected in the character of the fixed/recorded by thermogram thermal effect.

Consequently, specimen/sample 3 with stretching behaves simultaneously both energy- and entropy-elastic material.

However, an abbreviation in deformed specimen/sample 3, and also in specimen/samples 1 and 2 is accompanied by heat absorption (Fig. 116), i.e., after the assigned deformation, which leads to the decomposition of crystalline phase, to poly-urete it behaves as entropy-elastic material.

It is interesting that the more prolonged aging (four months) of specimen/sample 3 leads to a new change in the character of the thermal effects of its deformation (Fig. 116). In this case, as for specimen/samples with semimonthly aging, stretching is also

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accompanied by heat absorption; however, abbreviation occurs already,
on the contrary, with heat liberation.

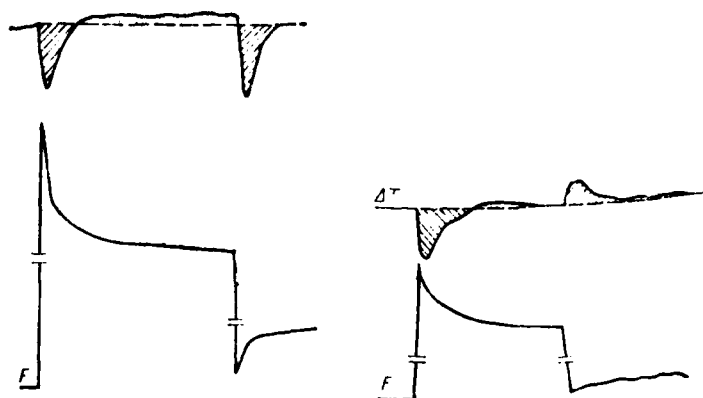


Fig. 115. Thermogram of the deformation specimen/samples 3, exposed/persistent two months at room temperature.

Fig. 116. Thermogram of deformation specimen/samples 3, exposed/persistent four months.

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This phenomenon is caused by further increase in the degree of crystallinity and perfection of the crystalline phase, which leads to the fact that the thermal effects of the deformation of polyurethane are determined already predominantly by the presence of crystalline phase.

Thus, basic process, calling endothermal effect during deformation, is elastic deformation. The nonconformity of the areas

of peaks with stretching and abbreviation is bonded with an abbreviation in the partially amorphized specimen/sample. It should be noted that the higher and more modern crystallinity of specimen/sample 3, exposed/persistent in the course of four months, indicate the increased values of voltage/stresses, corresponding to the same degree of stretching, as in the specimen/sample, exposed/persistent in the course of two months.

Since with this degree of stretching the decomposition of crystalline phase proceeds not so/such deeply, logically that it limits the development of highly elastic deformation. This escape/ensues from the absence of the clearly expressed exothermic effect after stretching, and also from the prevailing course of the exothermic process of the reversible elastic deformation during an abbreviation in the specimen/sample. Thus, specimen/sample 3 after four month old aging at room temperature behaves with stretching and abbreviation predominantly as an energy-elastic material.

From that presented it follows that an increase in cross-linked polyethyleneglycoladipateurethane of the length of oligoester block, conditioning the course in it of crystallization processes, leads to a change in the character of their deformation and molecular mechanism of this process. Character and mechanism of deformation for is polyurethane with sufficiently long oligoester blocks strongly it

depends on the depth of crystallization processes and perfection of the formed crystalline phase.

RELAXATION PROPERTIES OF POLYURETHANES.

Although many specific special feature/peculiarities it is polyurethane they are bonded with their relaxation behavior, works in this region it is small. Relaxation processes in polyurethane elastomers on three following reasons must differ from the same in other elastomeric systems the large contribution of physical reactions into effective network density; the possibility of the rearrangement of the structure of grid during deformation; the special feature/peculiarity of the structure of polyurethane chain, which is actually the molecule or block copolymer.

In numerous works according to mechanical properties, it is polyurethane they are brought the isolated information about stress relaxation in one or the other materials, but these results do still not give the presentation/concept of the special feature/peculiarities of relaxation behavior and its dependence on voltage/stress, effective network density, temperature, length and nature of oligomeric block, etc.

Meanwhile the study of this problem of the importantly not only understanding of specific character it is polyurethane, but also from the common/general/total positions of the theory of the viscoelasticity of reconstructing grids [135]. The chemical relaxation of polyurethane rubbers are bonded with the decomposition of the chemical bonds, which generate three-dimensional/space grid, and with caused by this factor relaxation of stresses [188, 282]. So, for six types of rubbers, in which are realized different bonds, are obtained the curves of the relaxation, from which are calculated the times of the chemical relaxation (see Fig. 63, Table 34). These data show that weakest weak bonds in polyurethane rubbers must be bonds of the type of disubstituted urea or biuret. The increase of the time of chemical relaxation with 120°C ten times can be reached during the replacement of these bonds to others. It was established that stress relaxation has identical speed both in the elastomers on the basis polyethers and in elastomers on the basis of polyesters, i.e., ester groups do not affect the rate of the relaxation of voltage/stresses [188, 282].

On low-modulus polyurethane composition with high transparency and double refractive sensitivity, is carried out the comparison mechanical and optical relaxation, based on the application/use of

principle of temperature-time superposition and theory of Williams-Landell-Ferri (WLF) [162]. For such specific and nonrepresentative in whole for it is polyurethane system they are calculated the value of relaxation module/modulus, factor is given a_T and other characteristics, determined by theory. The results of the comparison of experimental data will coincide with those calculated by the theory of WLF. Consequently, work shows the applicability of the theory of WLF to the systems of polyurethane series/number, but general regularities or special feature/peculiarities are not establish/installed.

Some dynamic mechanical properties are investigated for it is polyurethane on basis of poly - ϵ - caprolacton [202]. The study of mechanical losses at different temperatures will make it possible to connect them with molecular weight of polyester block. Interestingly that in this case is observed the peculiar dependence of mechanical losses on temperature (growth and achievement of maximum when T_c further decrease and again growth). In the region of higher than the temperature of the vitrification of polyether/polyesters of loss, they increase with the decrease of molecular weight.

Are prepared polyurethane in the form of homologous series in ratio/relation to the concentration of polar groups and to the density of nodes, and in the region of transition from glassy to

elastic state are investigated their viscoelastic properties. It is establish/installed, that the temperature of vitrification and the slope of the region of viscoelastic dispersion decrease with an increase in the concentration of urethane and biuret bonds and density of cross-linking. In each case reveal/detected large disagreement between the values and coefficients of the expansion of free space, calculated according to the theory of VLF and the equation of Doolittle (parameter B is accepted as unity).

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For the explanation of these disagreements, it is possible to assume that B decreases with temperature as a result of the thermal dissociation of the secondary bonds between polar groups, the lowering value of network element, which participates in molecular motion.

In work [280] are studied for the first time the relaxation properties of cross-linked ones it is polyurethane on the basis polyethers with purpose of connecting them with chemical nature and molecular weight of polyether/polyester, and also with the conditions of the synthesis reaction in the course of which is laid the structure of polyurethane. As objects are selected the cross-linked polyurethane on the basis of simple oligoester of different chemical

nature, 4,4'-diphenylmethanediisocyanate and trimethylol propane (TMP).

Obtaining is polyurethane it is possible to divide into two stages: synthesis of macro-diisocyanate and the formation of three-dimensional grid as a result of reacting MDI from TMP. For the synthesis of MDI, use PEG (mol. weight 500, 1000, 1500, 2000 and 3000), and also polyoxytetramethyleneglycol (PTGF, mol. weight 645, 960, 1450, 1930, 3000) and 4,4'-diphenylmethanediisocyanate, taken in relationship/ratio 1:2 [280]. Cross-linking it is polyurethane is conducted as a result of reacting MDI and TMP in the molar relationship/ratio NCO/OH=1.

On the relaxation properties of those cross-linked, it is polyurethane they judge by measurement data of relaxation of stress of film specimen/samples at the constant deformation of unidirectional tension and room temperature. For this purpose are remove/taken relaxation curves, from which are calculated the parameters of relaxation behavior according to the equation of Kohlrausch [250]

$$\sigma(t) = \sigma_{\infty} + \sigma_0 e^{-\left(\frac{t}{\tau}\right)^K} = \epsilon E_{\infty} + \epsilon E_0 e^{-\left(\frac{t}{\tau}\right)^K}, \quad (VII.3)$$

where $\sigma_{\infty}(E_{\infty})$ - an equilibrium part of the voltage/stress (modulus of elasticity); $\sigma_0(E_0)$ - the relaxing part of the voltage/stress

(modulus of elasticity); τ - relaxation time; ϵ - relative deformation of specimen/samples; K - constant of material.

Measurements conduct on relaxometer with the rigid dynamometer, ensuring the constancy of deformation during experiment, and by the automatic record of the measured values. Experimental value M_{∞} and $(\frac{v}{v})$, determine from equation (V, 1) by the values of the equilibrium modulus of elasticity E_{∞} , theoretical values M_{∞} and $\frac{v}{v} \big|_{\tau}$ calculate from equation (V, 2).

From the experimental curves of stress relaxation during constant deformation for two series of the specimen/samples of those cross-linked, it is polyurethane from different by network density (Fig. 117) employing procedure [105, 124] they are calculated the parameters of the equation of Kohlrausch.

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In terms of the obtained values of these parameters, are obtained the stress levels at different moment of times (point on graphs). As can be seen from Fig. 117, the calculated values satisfactorily coincide with experimental curves, which indicates the applicability of the equation of Kohlrausch for description of stress relaxation in the investigated polyurethane. Position and character of relaxation

curves show that the length of oligoester block in the investigated polyurethane grids has significant effect on the parameters of relaxation properties. Let us examine last/latter in more detail.

From the dependence of the equilibrium modulus of elasticity E_e from molecular weight of oligoester for it is polyurethane on the basis of PTGF and PPG (Fig. 118) is evident that a change in molecular weight of oligoester block exerts a substantial influence on the equilibrium modulus of elasticity. This is bonded with a change in the denseness of the three-dimensional/space grid, which depends on the length of oligoester link. An increase in molecular weight of oligoester block (decrease of network density) from 500 to 3000 leads to the gradual decrease of the equilibrium elasticity of three-dimensional/space grid 10-15 times.

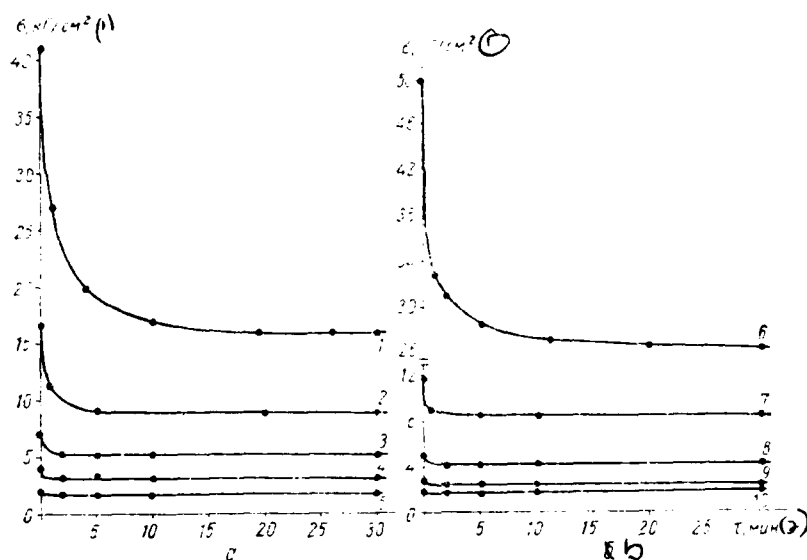


Fig. 117. Experimental the curves of stress relaxation it is polyurethane on the basis of PTGF (a) and PPG (b): 1 - with molecular weight 650; 2 - 960; 3 - 1450; 4 - 1930; 5 - 3000; 6 - 500; 7 - 1000; 8 - 1500; 9 - 2000; 10 - 3000.

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It should be noted that both curves are very close to each other, i.e., the equilibrium modulus of elasticity does not virtually depend on the chemical nature or the ether/ester component of those investigated it is polyurethane. This result will be in complete agreement with the conclusion/derivations of the kinetic theory of high elasticity according to which the elasticity of molecular

network is bonded only with network density.

In Fig. 118 it follows that for both it is polyurethane sharpest lowering in the equilibrium modulus it proceeds during an increase in molecular weight of oligoester block from 500 to 1500. Further increase M_{03} from 2000 to 3000 insignificantly decreases E_{∞} . From this it follows that at value $M_{03}=2000$ and above equilibrium elasticity does not virtually depend on the size/dimension of the oligoester comprising three-dimensional grid of polyurethane.

The kinetic parameters of the equation of Kohlrausch (relaxing part of the module/modulus or elasticity E_0 , relaxation time τ and parameter K) depend substantially on M_{03} (Fig. 119).

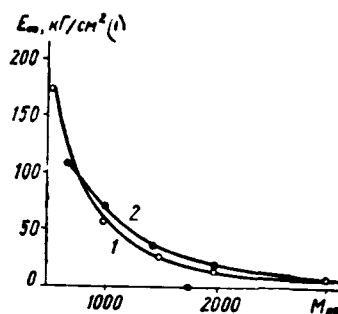


Fig. 118. The dependence of the equilibrium modulus of elasticity E_∞ on molecular weight of oligoester M_{03} , for it is polyurethane on the basis of PTGF (1) and PPG (2).

Key: (1). kgf/cm^2 .

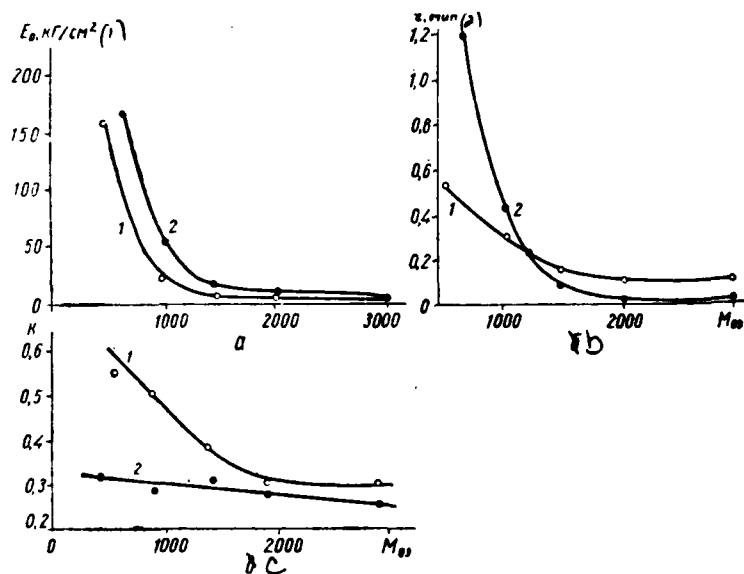


Fig. 119. Effect of molecular weight of oligoester M_{03} on relaxing part of module/modulus of elasticity E_0 (a), relaxation time (b) and

parameter K (b) for it is polyurethane on basis: 1 - PTGF; 2 - PPG.

Key: (1) . kgf/cm². (2) . min.

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However, in contrast to module/modulus E_0 , which proved to be insensitive to a change in the chemical nature of oligoester component, these parameters depend on the latter. The relaxing part of the module/modulus of elasticity E_0 (Fig. 119a) sharply decreases during an increase M_{03} for both it is polyurethane. In range of values M_{03} from 15000 to 3000, this is expressed weakly; however, E_0 for is polyurethane on the basis of PTGF considerably higher than corresponding values for it is polyurethane on the basis of PPG, especially in range of values M_{03} from 500 to 1000. This difference is gradually decreased with an increase M_{03} .

Although the modulus of elasticity for a polymer and is not the constant (it it depends on speed or duration of deformation), nevertheless this is the important characteristic of polymer, which makes large physical sense. It is the measure of three-dimensional/space of cross-linking of polymer. In terms of the values of the relaxing part of the modulus of elasticity, it is possible to judge the speed of the course of relaxation processes,

limited viscosity, etc. In connection with this we have made the attempt to obtain the analytical expressions of the bond of these parameters with molecular weight of oligoester link. For this, the dependences E_{∞} and E_0 on M_{03} (see Fig. 118 and 119a) are rebuilt in coordinates $\lg E_{\infty}$ ($\lg E_0 - \lg M_{03}$) (Fig. 120). It turned out that they have the linear character:

$$\begin{aligned}\lg E_{\infty} &= A - B \lg M_{03}, \\ \lg E_0 &= A_1 - B_1 \lg M_{03}.\end{aligned}$$

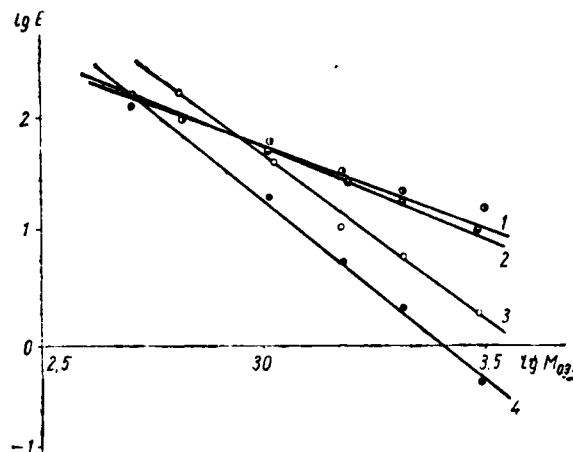


Fig. 120. Logarithmic dependence by equilibrium to E_{∞} (1, 2) and relaxing E_0 (3, 4) of the parts of the modulus of elasticity of M_{03} for is polyurethane on the basis of PTGF (1, 3) and PPG (2, 4).

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The determined from curves of Fig. 120 constants of equations comprise $A=6.03$; $B=1.42$; $A_1=10.44$; $B_1=2.93$ for is polyurethane on the basis of PTGF and $A=6.62$; $B=1.63$; $A_1=10.7$; $B_1=3.15$ for is polyurethane on the basis of PPG.

Molecular weight of oligoester affects also the relaxation time τ , which is the characteristic of the speed of the relaxation processes (see Fig. 119b). With an increase M_{03} relaxation time for both it is polyurethane sharply it descends in range of values

$M_{09} = 500-1500$, approaching equilibrium during further increase M_{09} . With M_{09} close to 1200, relaxation time and, consequently, also speed relaxation processes for both is polyurethane they are identical; lower than this value M_{09} relaxation time has greater value for polyurethane on the basis of PTGF, but it is higher than it - for polyurethane on the basis of PPG. Apparently, with molecular weight of oligoester more than 1200 becomes possible the ordering of the sections of the macromolecules between nodes for polyurethane grids on the basis of PTGF as a result of the more regular chemical structure of the latter.

Parameter K of equation reveals more critical dependence on M_{09} for it is polyurethane on the basis of PTGF, monotonically descending from 0.55 to 0.29 during an increase M_{09} from 645 to 3000. Its values for PU on the basis of PPG decrease linearly from 0.32 to 0.24 during an increase M_{09} from 500 to 3000.

Table 60. The experimental and theoretical values of average molecular weight of segment ($M_{c,s}$ and $M_{c,T}$) and of effective density of cross-linking it is polyurethane on the basis of PTGF and PPG.

M_{09}	$M_{c,s}$	$\left(\frac{v_e}{v}\right)_s \cdot 10^4$ <small>MOLE/CM³ (P)</small>	$M_{c,T}$	$\left(\frac{v_e}{v}\right)_T \cdot 10^4$ <small>MOLE/CM³ (P)</small>	$\left(\frac{v_e}{v}\right)_s / \left(\frac{v_e}{v}\right)_T$
ПТГФ					
650	774	14.30	1195	9.28	1.54
900	1320	8.05	1505	7.07	1.14
1450	2120	4.79	1995	5.10	0.94
1950	3465	2.86	2475	4.01	0.71
3000	6070	1.61	3545	2.77	0.58
ППГ					
500	508	23.0	1045	11.20	2.05
1000	1455	7.5	1545	7.07	1.06
1500	2690	3.8	2045	5.02	0.80
2000	4170	1.22	2545	3.92	0.57
3000	6085	1.5	3545	2.78	0.58

Key: (1) - mole/cm³.

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From the experimental values of equilibrium modulus and density ρ , is calculated molecular weight of segment M_{09} and effective density of cross-linking $\left(\frac{v_e}{v}\right)_s$ (table 60). For a comparison are represented theoretical values $M_{c,T}$ and $\left(\frac{v_e}{v}\right)_T$, determined according to equation (V, 2), on the basis of the stoichiometric relationship/ratios of the initial products, undertaken for synthesis is polyurethane.

As is evident, for both is polyurethane with small ones M_{OS} (500-1000) experimental values M_{OS} and $[\frac{V_e}{V}]$ will prove to be respectively less even larger than theoretical, but for was polyurethane with large M_{OS} (2000-3000) - conversely. This dependence, apparently, is bonded either with a change in the character of the defectiveness of chemical grid (for example, by transition from the lashing of chains into PUNO¹ whose action/effect analogous with the action/effect of the chemical bonds, to a large quantity of ne-cross-linked sections and ends of the chains for PUVO¹ which nothing they introduce into the elasticity of molecular network), or with the special feature/peculiarities of the supramolecular structure of these it is polyurethane.

FOOTNOTE 1. PUNO and PUVO - polyurethane on the basis of low-molecular and high-molecular oligoesters respectively.
ENDFOOTNOTE.

The discovered anomaly satisfactorily is explained with the positions of the supermolecular structures of those investigated it is polyurethane, which leads to the need for the examination of their mechanical behavior for close connection with conditions for synthesis and kinetics of the process of cross-linking.

Examining the obtained result from this position, it is possible to state/establish that the behavior of those investigated it is polyurethane with the large length of oligoester block bonded with the incompleteness of the formation of chemical grid. It is obvious, in this case of condition and the kinetic special feature/peculiarities of the process of cross-linking are such, that is impossible the realization of the complete cure of MDI in conformity with stoichiometry of initial products. Therefore the defectiveness of grid for data it is polyurethane it is characterized by a smaller number of cross-linkings per unit of volume, than it follows from theoretical considerations, and by a large number of free ends of the chains.

For explaining the reasons for the discovered anomaly conducted calorimetric investigation of kinetics of the process of cross-linking, which showed that the speed of the cross-linking of MDI decreases with an increase M_{03} . However, even in the case of high-molecular oligoester the duration of solidification does not exceed 6 h, that illustrates well the curve of the dependence of the parameter of the perfection of the process of cross-linking on the thermal effect of reaction on time (Fig. 121). Hence it follows that the selected by us time for solidification it is polyurethane

completely sufficiently and is not the reason for the incompleteness of the formation of grid.

T. E. Lipatova and S. A. Zubko have shown [61], that the formation of the grid of the point of gel formation is described by equation of Avrami [165].

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It is interesting to note that the value of the specific rate of formation of gel fraction K_0 , determined from this equation, correlates with the value of the equilibrium modulus of elasticity. For both of types, it is polyurethane to the high values K_0 they correspond and the high values of the equilibrium modulus of elasticity (Table 61). From these data it follows that between the parameters of relaxation properties and the characteristics of kinetics of the process of cross-linking it is polyurethane there is the specific bond. Therefore setting up of the investigations, dedicated to this bond, has large of value for explaining the special feature/peculiarities of the structure of polyurethane elastomers and explanation of the anomalies of their mechanical behavior.

For studying the structure at supramolecular level, carried out electron-microscope investigation (on electron microscope UEMV-100

according to the method of oxygen etching in gas discharge [9]) objects (Fig. 122, see insert), which showed that they possess globular structure. Similar globular structures are observed in the case of other polyurethane elastic systems of reticular structure [58], and also in cross-linked elastic polyalkylmethoxysiloxane [125], in cross-linked polyacrylates [37], phenol-formaldehyde and other polymers of spatial structure [34, 207, 319]. The globular structure of polymer networks is sufficiently distributed for many three-dimensional/space amorphous polymers both in glassy and in highly elastic states.

That establish/installed by us the deviation of the experimental values of the density of cross-linking ($\frac{v_c}{v}$), and of average molecular weight of the segment from them of the theoretical values (see Table 60) is possible satisfactorily to explain from the positions of the globular structure of the investigated polyurethane grids.

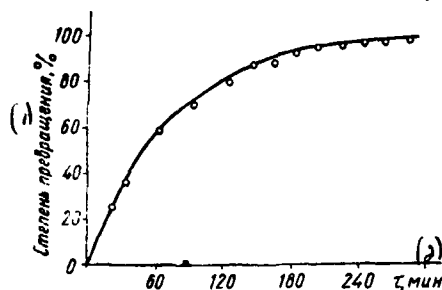


Fig. 121. Kinetic curve the formation of polyurethane grid on the basis of PPG of molecular weight 2000 at the temperature of cross-linking by 80°C.

Key: (1) . the degree of transformation. (2) . min.

Table 61. The kinetic parameter of the process of cross-linking and the equilibrium modulus of elasticity for are polyurethane on the basis of PTGF and PPG.

M_c, g	$K_c \cdot 10^3, \frac{min^{-1}}{g}$	$E_{\infty}, \frac{kg}{cm^2}$ (2)
ПТГФ		
960	7.98	71
1930	5.40	20
ППГ		
500	13.60	168
2000	5.79	16

Key: (1) . min^{-1} . (2) . kg/cm^2 .

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Really/actually, during obtaining of PUNO, are formed the globules of smaller size/dimensions than in the case of PUVO, that confirm the electron-microscope observations. For small globules in comparison

with large-globular structure, there is large probability that NCO-group, which participate in the reaction of cross-linking, are arrange/located on their surface or near it. In large-globular structure the arrangement of reactive NCO-group is more probably within the volume of globules, than on their surface, as a result of high size/dimensions. This leads to the formation of defective grid with a large quantity of unreacting functional groups, and consequently, with a large number of free ends of the chains of grid. Thus, incomplete solidification and incompleteness of the formation of chemical grid in PUVO is a result of their globular structure.

And finally, in the examination of the special feature/peculiarities of the structure of the investigated by us grids and their bond with mechanical behavior it is necessary to take into consideration the position of the urethane groups in grid, which are the main reason for strong physical reaction. It is obvious, the urethane groups, arrange/located in chemical network points, have smaller possibility for the formation of hydrogen bonds, since their mobility is suppress by strong chemical bonds. However, the degree of the collaboration of these groups in the formation of physical bonds is changed upon transfer from PUVO to PUVO. Really/actually, in the case of application/use for the synthesis of low-molecular oligoester, is formed the polyurethane fine-globular structure, which has more developed interface, which conditions a stronger physical

reaction between globules with a maximally possible (for the given size/dimension of globules) denseness of the chemical grid, which approaches theoretical. In spite of the fact that urethane groups "are enslaved" in chemical network points, their possibilities in the formation of hydrogen bonds to the certain degree grow/increase because of a large quantity of adjacent small/fine globules. This, apparently, and leads to the larger experimental values of the equilibrium moduli of elasticity, effective density of cross-linking and the smaller values of average molecular weight of segment, in comparison with theoretical for PUHO.

With the synthesis of PUVO, is formed the chemical grid with more appreciable globules, which possesses much smaller interface. In connection with this occurs incomplete solidification it is polyurethane and the formation of more defective chemical grid with a smaller quantity of chemical bonds per unit of volume. Furthermore, the value of physical reaction is minimum due to a smaller quantity of physical contacts between more appreciable globules and smaller possibilities for the formation of hydrogen bonds, by the "enslaved" in chemical nodes urethane groups.

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Consequently, in this case the contribution and chemical, and

physical reactions into equilibrium elasticity is minimal, than are explained the obtained by us considerably lower experimental values of the equilibrium modulus of elasticity, effective density of cross-linking and the higher values of average molecular weight of segment in comparison with theoretical ones.

The chemical nature of oligoester block does not virtually affect the equilibrium elasticity (see Fig. 118, Table 60), and also average molecular weight of segment and effective density of cross-linking; however, is had noticeable effect on kinetics of relaxation process (cm, Fig. 119).

Thus, the study of the relaxation properties of cross-linked ones it is polyurethane on the basis polyethers in connection with by their molecular and supermolecular structures and conditions for obtaining it will make it possible to establish/install some special feature/peculiarities of structure and mechanical properties. During an increase in the length of oligoester block, decrease chemical and physical reactions and, consequently, also equilibrium elasticity, which is caused by the globular structure of polyurethane grids.

The obtained results show that the chemical grid of those investigated it is polyurethane it is characterized by the significant structural heterogeneity, which exerts a substantial

influence on the mechanical behavior of polymeric body. Therefore it is necessary to reexamine the mechanical conducting of such systems on the basis of the new presentation/concepts of their globular structure.

The results of this investigation are related to polyurethane, in which the role of physical bonds is relatively small. Meanwhile interest is in relaxation, bonded also with decomposition and reduction of physical network points. Such processes to a certain degree are analogous to chemical relaxation. From this point of view, it is important the study of the linear amorphous "meristic" elastomers in molecules of which there is a sequence of pliable and rigid segments [193]. In such elastomers large strength and high modulus of elasticity are higher than the temperature of vitrification T_g , where other elastomers had properties of viscous liquids. The authors [193] assumed that the rigid segments play the role of fillers and cross connections. The region of the increased moduli of elasticity between T_g and the temperature of the vitrification of the bonded rigid segments T_g' is caused by the association of glassy blocks of elastomers. Based on the example of polyesterurethane, which contains plasticizer (polyethylene glycol with a mol. weight of 200), it is shown, that the latter solvates predominantly the segments of polyether/polyester and it descends T_g without decreasing the modulus of elasticity above T_g . If we take dimethyl sulfoxide, then

it solvates rigid segments, lowering the module/modulus between T_g and T_c . For such systems were investigated viscoelastic properties and temperature dependence of module/modulus.

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In their time Bartenev and Vishnitskaya [8] investigated the relaxation properties of filled rubbers and established that stress relaxation in them is determined by three processes - relaxation of chains, relaxation, bonded with the breakaway of the chains of rubber from the particles of the filler, and by the rearrangement of very particles of the filler. Returning to polyurethane, it is possible to assume that in them really/actually must be realize/accomplished the processes, bonded with the relaxation of physical nodes (to equivalent bonds rubber - filler in common rubbers). Such processes are really/actually reveal/detected during the study of dielectric and spin-lattice relaxation in oligomers and polyurethane [76]. As objects are selected oligohydroxytetramethyleneglycol, oligodiethyleneglycoladipate and adduct on the basis of trimethylol propane and TDI, and also polyurethane on the basis of oligodiethyleneglycoladipate and dimer of TDI, oligohydroxytetramethyleneglycol and oligodiethylene glycol and mentioned above adduct.

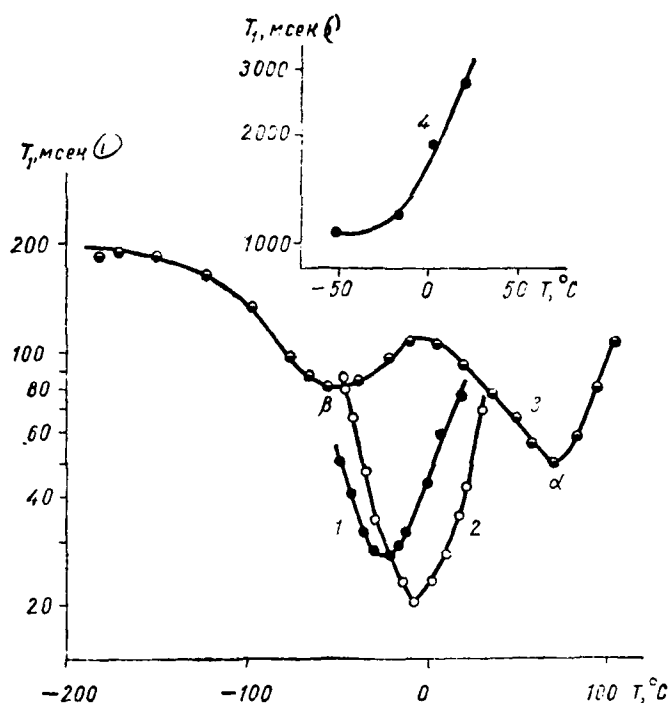


Fig. 123. The dependence of the time of spin-lattice relaxation on the temperature: 1 - oligoxyhydroxytetramethyleneglycol; 2 - oligodiethyleneglycoladipate; 3 - adduct on the basis of trimethylol propane and TDI; 4 - cyclonhexanone.

Key: (1). ms.

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Figure 123 depicts the temperature dependence of time T_1 of the spin-lattice relaxation of protons for

oligohydroxytetramethyleneglycol, oligodiethyleneglycoladipate and adduct on the basis of trimethylol propane and toluenediisocyanate, but also for pure/clean cyclonexanone, since in its adduct being investigated are contained about 300/o. As is evident, for polyether/polyesters is observed one relaxation process: for polyether with -25°C , for complex - with -8°C . It is known, [96], that in oligomeric molecules is developed its own flexibility of chain. Since polyether/polyesters being investigated are linear and do not contain lateral and CH_3 -group, then is obvious that the existing relaxation process is bonded only with the motion of the segments of molecular chains; their mobility is greater for oligohydroxytetramethyleneglycol, than for oligodiethyleneglycoladipate. The retardation of the motion of the molecules of polyester is explained by the presence in the chain of the additional polar groups, which lead to more strong/durable structural physical grid. Table 62 corrected values of the energies of the activation of relaxation process.

Adduct is characterized by two (α and β) relaxation processes (Fig. 123, curve 3) at 70 and -48°C , caused by the motion of the associates of two types, which develop relaxation at higher and lower temperatures. For α - process is observed the break in the curve of dependence $\tau_c = \tau(1/T)$, moreover straight line with smaller slope/inclination is virtually parallel to the appropriate straight

line for a β -transition and it differs little from the slope/inclination of straight line for cyclohexanone (Fig. 124), which gives virtually the identical energies of activation (2.4; 2.57; 2.95 kcal/mole, Table 62). If one considers that the β -transition of adduct and relaxing of cyclohexanone occur/flow/fast almost at identical temperatures (-48 and \sim -52°C), then it is obvious that β - process and dependence $\lg \tau_c = \varphi \frac{1}{T}$ with smaller slope/inclination they are caused by the presence in the adduct of cyclohexanone, but α -process is caused by the molecular mobility of the associates, formed because of the presence in the adduct of a large quantity of urethane and other groups.

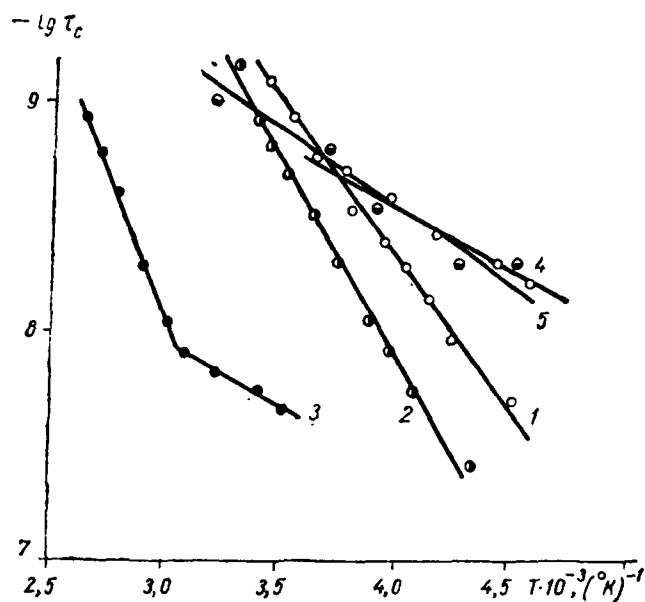
Table 62. Values of the energy of the activation (kcal/mole) of initial components.

Компонент (1)	Движение сегментов (2)	α -Процесс (3)	$T_{мин}$, °C
(4) Простой ПЭ	6,10	—	—25,5
Сложный ПЭ (5)	7,34	—	—8,0
Аддукт (6)	—	13,75 (2,57)	—70,0
			—48,0
Циклогексанон (7)	—	2,95	—52

Key: (1). component. (2). motion of segments. (3). process. (4). simple. (5). complex. (6). adduct. (7). cyclohexanone.

Note. The energy of the activation of β - process of adduct is equal to 2.4 kcal/mole.

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Fig. 124. Dependence $lg \tau_c$ on $1/T$: 1 -

oligohydroxytetramethyleneglycol; 2 - oligodiethyleneglycoladipate; 3

- α - process of adduct; 4 - β - process of adduct; 5 - cyclohexanone.

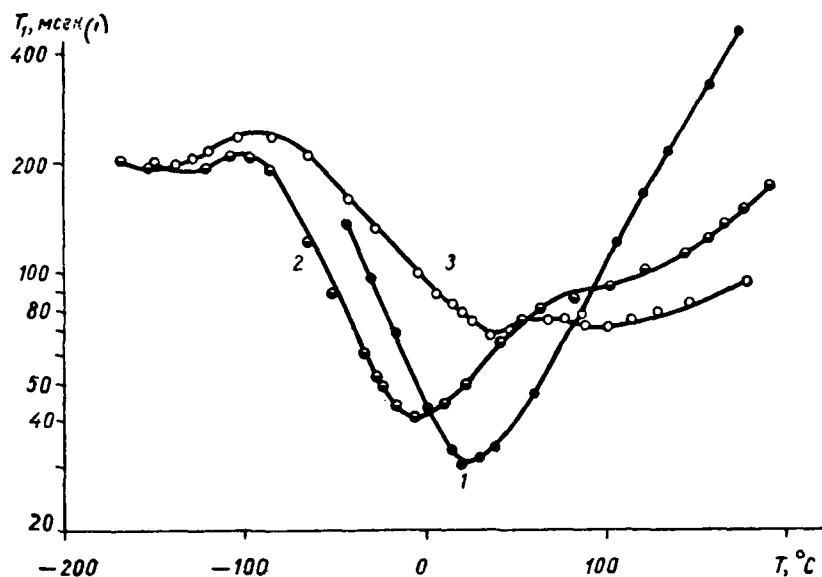


Fig. 125. Dependence of time of spin-lattice relaxation on temperature: 1 - PU rubber; 2 - PU on basis simple PE; 3 - PU on basis complex PE.

Key: (1) . ms.

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From the temperature dependence of the time of spin-lattice relaxation T_1 (Fig. 125) is evident that for those investigated are polyurethane it is observed three relaxation processes: low-temperature (from -138 to -141°C), bonded with motion CH_3 -group; the process, caused by segmental mobility of chain; for polyurethane

rubber (20°C) of polyurethane on the basis simple PE (-10°C) and polyurethane on the basis complex PE (35°C), and also process at the higher temperatures, which presents for polyurethane systems the special interest. If for polyurethane rubber (Fig. 125, curve 1) of this transition it is not observed, then already for PU on the basis simple PE (curve 2) there is a tend - weakly expressed minimum of relaxation which is well visible for it is polyurethane on the basis complex PE (curve 3). The energy of the activation of this process two times exceeds the same for segmental movement and is 4.29 kcal/mole (Table 63). This process can be caused by the redistribution of molecular bonds and by the mobility of the nodes of physical three-dimensional grid, that it is possible to present as follows: with an increase in the temperature in the field of the superimposed perturbing loads, the part of the segments of chains, bonded by the nodes of three-dimensional physical grid, is free/released, in consequence of which are formed new nodes and is developed the mobility of sufficiently large structural units.

Apparently, this process is impossible to relate to decomposition or possible rearrangement [114] of biuret, allophanate and uric groups, since for their rearrangement is required the activation energy from 20 to 50 kcal/mole, and, according to [254], dissociation of biuret it becomes noticeable only with 120, allophanates - at 106°C. According to data [294], the biuret react

with amines with 150°C. The results of the investigation of dielectric relaxation (Fig. 12b) show that relaxing the nodes of physical three-dimensional grid at frequency 10 Hz occurs at 40-50°C (curve 2) for it is polyurethane on the basis simple PE, 45-75°C (curve 3) for is polyurethane on the basis complex PE and it is not developed for polyurethane rubber (curve 1).

Table 63. The values of the energy of activation (kcal/mole) it is polyurethane.

Полиуретан (1)	Движение групп (2)	Движение сегментов (3)	α -Процесс (4)	β -Процесс (5)
ПУ каучук (6)	—	5.95	15.00	—
ПУ на основе простого ПЭ (6)	0.8	4.38	8.24	13.25
ПУ на основе сложного ПЭ (7)	1.1	2.05	18.80	21.0

Key: (1). polyurethane. (2). motion of groups. (3). motion of segments. (4) / process. (5). rubber. (6). on basis of simple. (7). on basis of complex.

Note. The energy of the activation of the motion of nodes for polyurethane on the basis of polyester is equal to 4.3 kcal/mole.

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For polyurethane rubber take the place two processes of the dielectric relaxation: dipole- segmental at -20°C and dipole- group at -95°C . It is known that the region of relaxing of segments and chains (α -absorption) for it is polyurethane it is observed approximately at -40°C [150, 234, 235]. Upon transfer from polyether/polyester to the appropriate polyurethane, occurs the displacement of dielectric relaxation to the side of positive temperatures (in this case of -20°C). Analogously for the

spin-lattice relaxation of polyurethane rubber (see Fig. 125, curve 1) displacement composes 31°. For those cross-linked it is polyurethane also it occurs the displacement of the spin-lattice relaxation of segments to the side of high temperatures in comparison with transition for polyether/polyesters, but this displacement considerably does not exceed the temperature of the high-temperature relaxation process of adduct (Table 64).

Thus, the relaxation of segments in polyurethane is developed at the temperatures, which exceed the temperature range of relaxing corresponding initial polyether/polyesters, but it does not exceed the same of the high-temperature relaxation process of adduct. This is bonded with the decrease of mobility as a result of the cross-linking of pliable oligomeric chains by the rigid associates of adduct, by a change in the value of kinetic segment and, in essence, with the formation of structural physical grid, since the shift of the region of relaxation for is polyurethane on the basis complex PE almost three times more than shift for polyurethanes on the basis of simple PE (Table 64).

Examining now dielectric relaxation for those cross-linked it is polyurethane (Fig. 126, curve 2 and 3), it is possible to say that dipole-segmental process must be revealed in the temperature range of higher than -40°C at the frequencies of below 100 Hz.

Table 64. Shift of the minima of spin-lattice relaxation processes upon transfer from polyether/polyesters to the appropriate polyurethane.

Наименование (1)	$T_{\text{мин}}, \text{K}$	Смещение по отношению к полиэфир-у, град (2)	Смещение по отношению к аддукту, град (3)
Простой ПЭ	247,5	—	—
ПУ на основе простого ПЭ (4)	263	15,5	80
Сложный ПЭ (5)	265	—	—
ПУ на основе сложного ПЭ (6)	308	43,0	35

Key: (1). designation. (2). shift with respect to polyether/polyester, deg. (3). shift with respect to adduct, deg. (4). simple. (5). on basis of simple. (6). complex. (7). on basis of complex.

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From the results of the investigation of α - process, it is evident that for polyurethane rubber the transition is observed at -95°C , for is polyurethane on the basis simple PE with -120°C and for is polyurethane on the basis complex PE with -108°C . Furthermore, in the cross-linked polyurethane occurs another β - process (for polyurethane on the basis simple PE with -65°C and for polyurethane on the basis of complex PE with -75°C), which can be explained by the motion of kinetic unity (groups of atoms), which have the size/dimensions of

more than those that are heavy-duty/critical for dipole-group motion, but are less than the size/dimensions of the segments of chains.

Thus, if for polyurethane rubber, as for the other linear noncrystallizing polymers, is observed only two processes of dielectric relaxation, then in the cross-linked polyurethane their quantity is increased because of the presence of the wider spectrum of kinetic unity.

From Fig. 127 it is evident that the slope/inclination of dependence $\lg \tau_c = q \left(\frac{1}{T} \right)$ PU being investigated decreases upon transfer from linear to the cross-linked polyurethane on the basis complex PE.

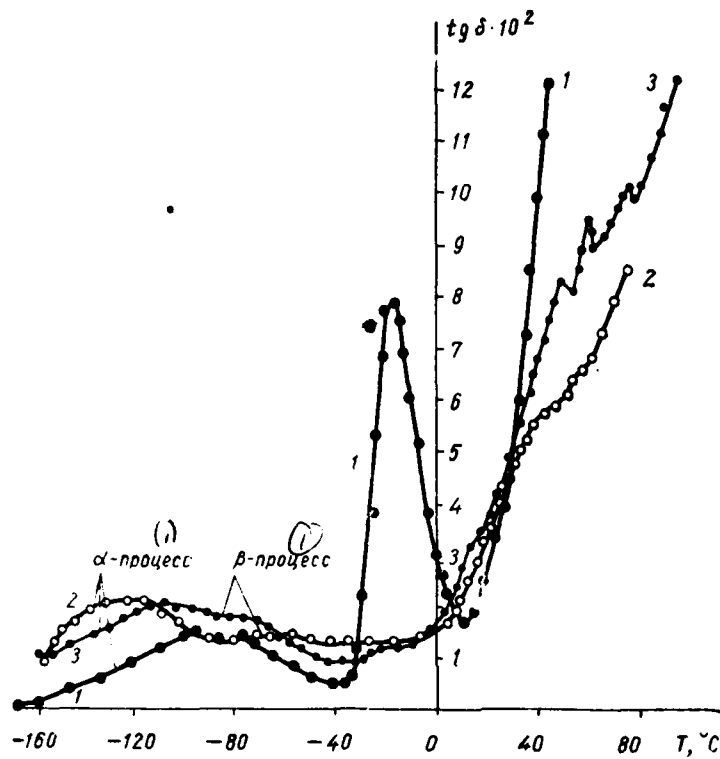


Fig. 126. Temperature dependence $\text{tg } \delta$: 1 - PU rubber; 2 - PU on the basis of simple PE; 3 - PU on the basis complex PE.

Key: (1). process.

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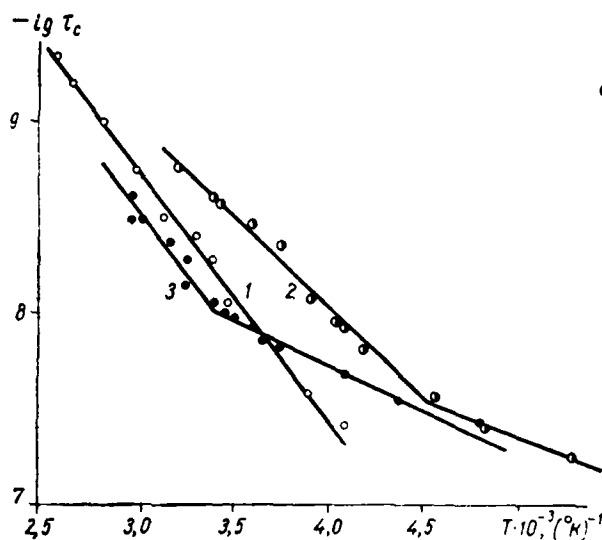


Fig. 127. Dependence $\lg \tau_c$ on $1/T$ for segmental movement of spin-lattice relaxation: 1 - PU rubber; 2 - PU on basis simple PE; 3 - PU on basis complex PE.

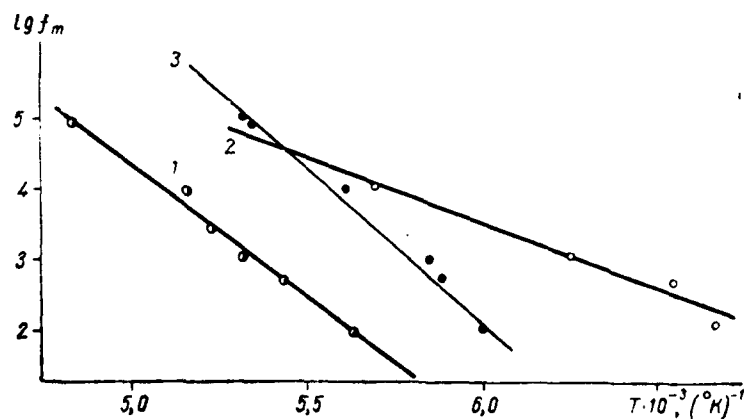


Fig. 128. The dependence $\lg f_m$ on $1/T$ for α -process: 1 - PU rubber; 2 - PU on the basis simple PE; 3 - PU on the basis complex PE.

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The decrease of the energy of the activation (see Table 63) can be explained by expansion of the spectrum of the relaxation times of kinetic unity in the cross-linked polyurethane and, therefore, by the decrease of the energy barrier of activation. Figure 128 depicts also dependence $\lg f_m = \varphi\left(\frac{1}{T}\right)$ for α - process of dielectric relaxation.

Thus, relaxation behavior of polyurethane is really/actually defined by both the flexibility and properties of oligomeric block and by presence of the rigid units and of the nodes of physical grid. This typically also for those filled it is polyurethane.

Dielectric relaxation in polyurethane is investigated also for purpose of the determination of the character of a change in intermolecular interactions upon transfer from polyether/polyesters to polyurethane and the determination of their temperatures of vitrification [151]. Strictly the mechanism of relaxation processes the authors do not examine, but findings will give the foundation for connecting the manifestation of the forces of intermolecular interactions (physical network points) with the formation of the

bonds between polar CO-groups in ester polyurethane and with the hydrogen bonds between urethane groups for was polyurethane on the basis polyethers.

We will examine the relaxation phenomena in the polyurethane elastomers, containing pliable units.

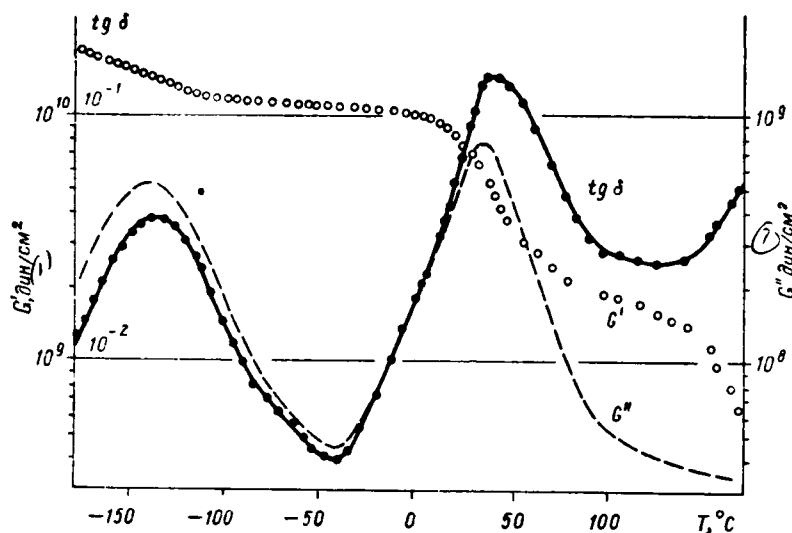


Fig. 129. The temperature dependence of the real and imaginary parts of the complex module/modulus (G' and G'') and of the mechanical losses $\text{tg } \delta$ at frequency 1 Hz for polyurethane on the basis of 1,4-butanediol.

Key: (1) - dyn/cm².

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However, interest are of the relaxation properties of linear ones it is polyurethane on the basis of low-molecular diols, for example on the basis of hexamethylene diisocyanate and 1,4-butanediol, 1,6-hexanediol, 1,10-decanediol and 2,5-hexanediol [238]. The data of

the dependences of mechanical losses and module/moduli G' and G'' on temperature for polyurethane on the basis of 1,4-butanediol give two region of relaxation with -135°C (γ - maximum) and to $+40^{\circ}\text{C}$ (main or α - maximum) (Fig. 129). The first is caused by the mobility of CH_2 -group, and the main thing corresponds to the temperature of devitrification, i.e., to the beginning of micro-Brownian mobility of chain in amorphous zones.

An increase in the losses and a strong incidence/drop in the module/modulus are higher than 150°C bonded with melting of the crystalline regions of polymer. The temperature dependences of losses for it is polyurethane the basis of different diols (Fig. 130) they indicate the shift of the temperature position of principal maximum approximately on 5°C during an increase in the length of chain by two carbon atoms. The authors treat their results on the basis of the presentation/concepts of hydrogen bridges in the amorphous zones of those investigated it is polyurethane, which act as cross connections.

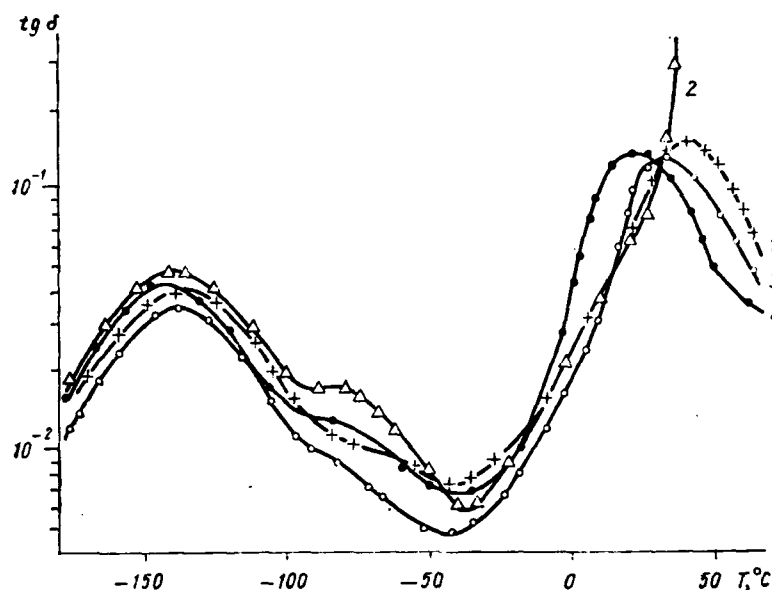


Fig. 130. The temperature dependence of the mechanical losses $\text{tg } \delta$ for it is polyurethane on the basis of hexamethylene diisocyanate and different glycols: 1 - 1,4-butanediol; 2 - 2,5-hexanediol; 3 - 1,6-hexanediol; 4 - 1,10-decanediol (frequency 1 Hz).

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In this case, the elongation of chain decreases a number of hydrogen bonds by the unit of length of chain, in consequence of which grow/increases the flexibility and is changed relaxation behavior.

Is investigated the effect of thermal previous history on the position of the maximum of losses and its time/temporary dependence

with constant temperature [238]. The changes, which in this case occur, were bonded with crystallization, that, in particular, it will make it possible to examine also isothermal crystallization in the terms of equation of Avrami from dependence $\lg t g \delta$ on time.

FLOW PROPERTIES OF OLIGOMERS.

Many most important properties it is polyurethane they are determined by the same of the oligomeric units (for example, see data on vitrification, flexibility, etc.). By this is explained interest in the study of oligomeric systems. The significant contribution to understanding of behavior is polyurethane we can introduce the rheological investigations of oligomers. This region is developed very little. In this section we will attempt to show the interrelation between the flow properties of oligomers and properties it is polyurethane.

Yu. S. Lipatov and coworkers will establish/install for the first time some essential anomalies of the rheological behavior of oligomers [66]. They investigate the flow properties of some oligomeric polyether/polyesters, which were being used for the synthesis of polyurethane elastomers. As objects are selected polytetrahydrofuraneoxypropyleneglycols with a molecular weight of by 1000 and 2000 (content of propylene oxide in copolymer 20-25o/o) and

polyesters - polydiethyleneglycoladipate with molecular weights of 790 and 2050, and also polydiethyleneglycoladipinatetrimethylpropane (desmophen) with a molecular weight of 2200. Furthermore, are studied the concentrated solutions or the oligomers indicated in acetone (concentration 70, 80 and 90o/o). The ductility/toughness/viscosities of oligomers are measured in the range of temperatures of 20-60°C, and their solutions - at 20-30°C on rotational viscometer in the range of shearing rates from $4 \cdot 10^{-4}$ to $1.5 \cdot 10^2 \text{ s}^{-1}$ (Fig. 131).

Analyzing the shape of the curve of ductility/toughness/viscosity, it is possible to establish that all systems are characterized by the analogous course by rheological curve, on which it is possible to separate three sections: AB - the ascending branch of anti-thixotropy or structuring, BC - the region of the decomposition of structure, also, in certain cases - branch CD - zone of flow with the destroyed structure with constant ductility/toughness/viscosity. Depending on the type of oligomer and temperature of experiment, the individual sections of curves are expressed less or more clearly. In certain cases the part of the sections is misaligned according to the scale of shear stresses beyond the limits of the investigated region.

The discovered anomalous shape of the curve of ductility/toughness/viscosity is explained as follows.

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In section AB under the action/effect of the shift voltage/stresses of the molecule of oligomer, they are oriented relative to each other and as a result of strengthening or the reaction of the oriented molecules, appears the determinate structure. This process is analogous examined in [62, 219, 239] and can be named anti-thixotropy. During further increase in the shear stress, beginning with critical value P_{kp} , occurs the decomposition of structure (section BC) and then is realized the flow of completely destroyed structure (section CD), which in certain cases possesses greater ductility/toughness/viscosity than reference system at point A.

Consequently, with small shear stresses oligomers develop the anomalous ductility/toughness/viscosity in the field of transverse gradient, which reminds an increase in the effective ductility/toughness/viscosity with the superposition of shift and longitudinal flow [66].

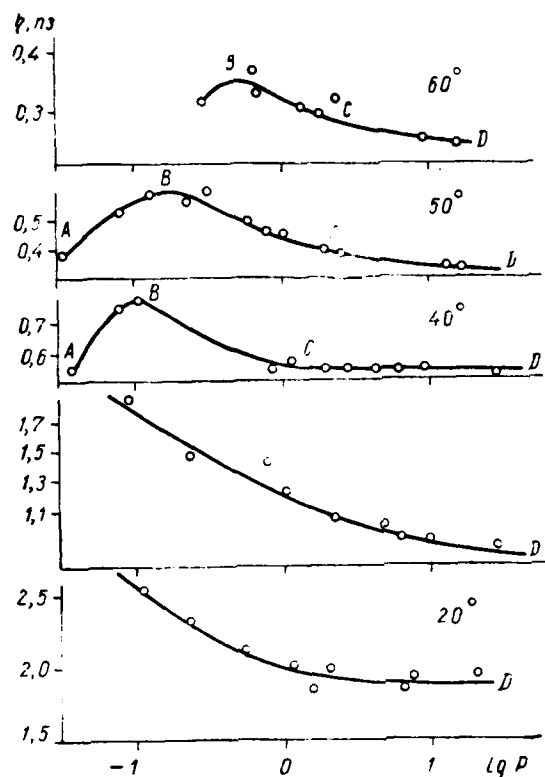


Fig. 131. Rheological curves of polydiethyleneglycoladipate (mol. weight 790).

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The analysis of other analogous curves shows that the effects of viscosity abnormality are expressed more sharply for the oligomers of smaller molecular weight. This, possibly, it is bonded with the increased hardness and the greater mobility of more short chains. For low-molecular systems structure formation occurs in proportion to an

increase in the temperature, beginning with higher shear stresses, as one would expect, taking into account the thermal agitation of molecules, but the decomposition of structure begins at higher values P_{kp} (for example, in Fig. 131 at 20 and 30° branch AB is not developed, but there is only section BCD).

In system with large molecular weight, branch AB appears already at room temperature. A change in molecular weight of oligomer leads to a change in the dependence P_{kp} on temperature. For a low-molecular oligomer P_{kp} it increases with an increase in the temperature, while for higher-molecular - it falls. Similar pattern is observed for two polyesters of different molecular weights. Finally, for the branched oligomer - desmophen - a temperature rise leads to decrease P_{kp} .

Such changes P_{kp} with temperature can be bonded with differences in orientation and flexibility of small and large molecules of oligomers. It is completely probable that in the first case occur only effects of orientation, whereas for higher-molecular specimen/samples have already been developed and deformation [149].

Let us pause now at the ductility/toughness/viscosity of the concentrated acetone solutions of oligomers (Fig. 132). In the more concentrated solutions of viscosity abnormality, they are retained, while a reduction in the concentration or an increase in the

temperature leads to their degeneration (up to transition to Newtonian flow). For the higher-molecular specimen/samples of viscosity abnormality, they are retained during high dilution.

It is obvious, viscosity abnormalities are bonded not simply with the orientation of molecules in flow, but also with the associated strengthening of the reaction between them. Findings cannot be explained by the unwinding of chains in the field of longitudinal gradient, as this is observed in [62, 219], because the possibilities of changing the conformations in the molecules of oligomers are considerably less than in high-molecular polymers. Furthermore, if anomalies were bonded with the deformation of oligomeric molecules, they brighter were expressed for higher-molecular specimen/samples.

These results indicate the need for the account the anomalies of the flow properties of oligomers with processing/treatment and synthesis of polymers. From them it also follows that intermolecular interactions between oligomeric units exert a substantial influence on the properties of the polymers, obtained on their basis. It is possible, this will make it possible to explain some properties it is polyurethane, for which usually are considered only intermolecular interactions, determined by the formation of hydrogen bonds.

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It is until recently considered that the highly elastic deformation was inherent only in high-molecular polymers, and high elasticity is considered as one of the signs of polymers. The low molecular polymers, which are located under normal conditions in viscous flow state, do not develop the specific properties of polymers and on the basis of this sign they are separate/liberated into the group of oligomeric compounds. Their molecular weight usually is within the limits of molecular weights of the mechanical segments of macromolecules.

Is investigated in detail the deformation behavior of such oligomer whose molecular weight coincides or close to values not of the mechanical segment of polymer [146]. As objects are selected two specimen/samples of the polyesters: linear polyether/polyester on the basis of adipic acid and diethylene glycol with a molecular weight of approximately 2000 (1) and branched polyether/polyester of the type desmophen with molecular weight approximately 2500 (2).

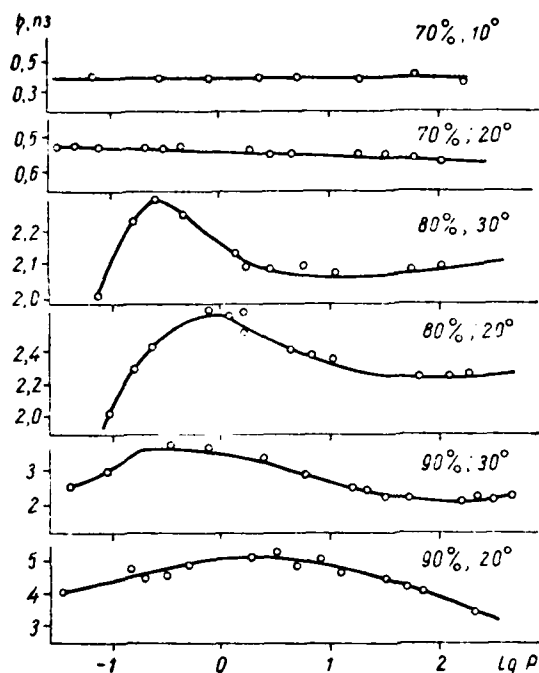


Fig. 132. Rheological curves of the concentrated acetone solutions of polydiethyleneglycoladipate (mol. weight 2050).

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The deformation behavior of the oligomers indicated is studied according to the method, based on kinetics of the development of the deformation of infinite shift/shear in the narrow gap of coaxial cylinders [111]. Investigation is reduced to obtaining of family of curves $\epsilon = \varphi(\tau)_t$ at shear stresses 3.6-43.8 dyn/cm² and temperatures of 20-70°C (Fig. 133).

Curves 1, 2 (Fig. 133a, b) correspond the conditions for explicit plastic flow with the low section, which corresponds to elastic deformation and with the significant portion/fraction of residual deformation after the removal of load at point $P=0$.

In proportion to growth P (curves 3, 4; Fig. 133a, b) is observed an increase in the portion/fraction of elastic deformation with the degeneration of straight portion by curve, that corresponds to plastic flow, i.e., the phenomenon, contradictory what occurs in dispersal systems and structured liquids [111, 112].

With an increase in the temperature to 50 and 60°C, system loses yield despite all the assigned conditions of deformation, and curves $\epsilon = \varphi(\tau)_P$ correspond to the deformation model of the outline/contour of Kelvin (Fig. 133c).

From rheograms for oligomer 2 (Fig. 134) it is evident that with shear stresses 21.9-36.5 dyn/cm² the given curves are analogous by curve 1, 2 Fig. 133.

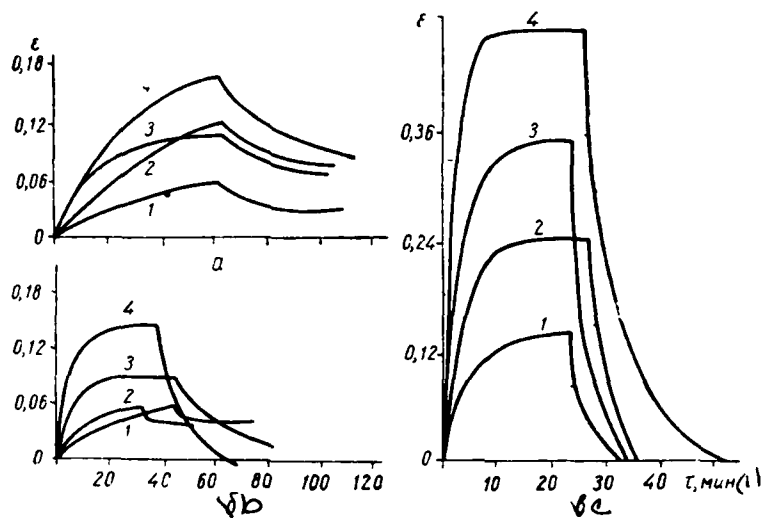


Fig. 133. Dependence of kinetics of the development of shearing strain for complex linear polyether/polyester with different shear stresses (dyn/cm²):

a - $t = 20^\circ\text{C}$; 1 - 3.65; 2 - 7.30; 3 - 10.95; 4 - 14.60; b - $t = 40^\circ\text{C}$; 1 - 3.65; 2 - 5.11; 3 - 7.30; 4 - 14.60; c - $t = 60^\circ\text{C}$; 1 - 7.30; 2 - 14.60; 3 - 29.20; 4 - 41.8.

Key: (1) . min.

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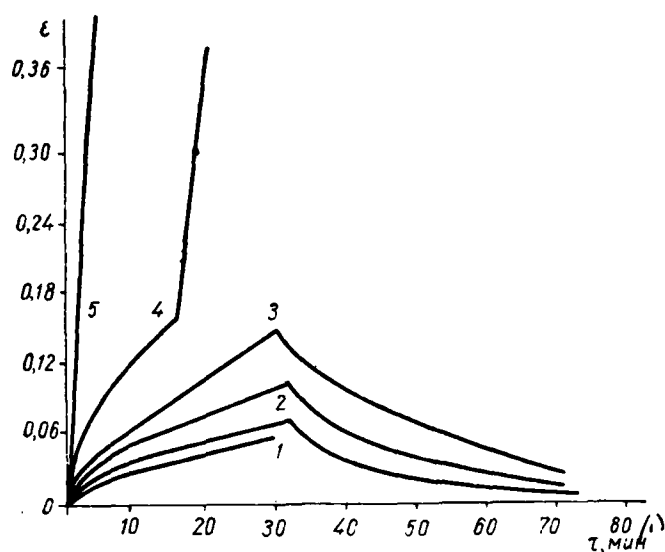


Fig. 134. Dependence of kinetics of development of shearing strain for complex branched polyether/polyester at temperature of 20°C and with different shear stresses (dyn/cm^2):

1 — 21.90; 2 — 29.20; 3 — 36.50; 4 — 48.80; 5 — 51.10.

Key: (1). min.

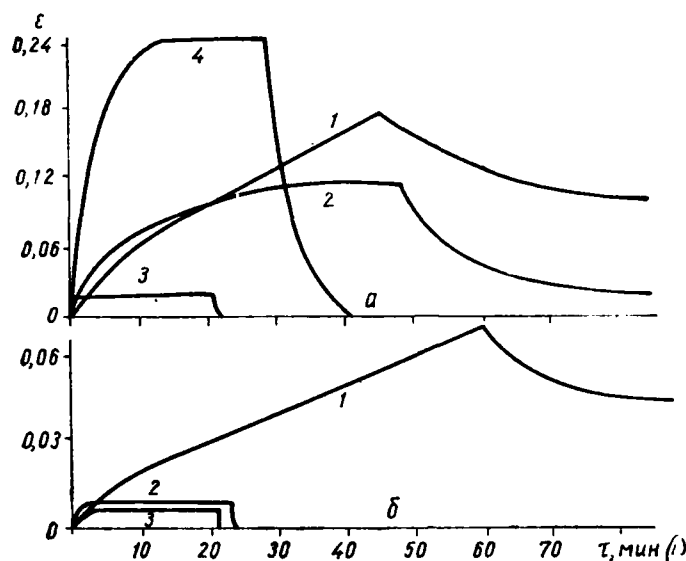


Fig. 135. Dependence of kinetics of the development of shearing strain for polyether/polyester 1 with $P=7.30$ (a) and 14.60 (b) dyn/cm^2 , 5 h and different temperatures:

1 — 20; 2 — 30; 3 — 50; 4 — $t = 60^\circ \text{C}$.

Key: (1). min.

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However, during an increase in the shear stress to 43.8 dyn/cm^2 , occurs brittle break in contrast to linear polyether/polyester, for which with increase of P was increased the portion/fraction of elastic deformation (curves 3, 4 Fig. 133). With an increase in the temperature, the strength or structure decreases and it disintegrates

respectively at the smaller values of shear stresses as this shown below:

$T, ^\circ\text{C}$	20	30	40	50	70
P_p	43,8	36,5	29,2	21,9	14,6

For the development/detection of the structural units, which are determining the deformation behavior of the systems indicated, is determined the effect on the elastic properties of the latter of the stress level of shift/shear, temperature and heating time.

It is shown, that in the range of temperatures of 20-50°C for specimen/sample 1 the elastic deformation decreases with an increase in the temperature and respectively is increased elasticity modulus under the condition of taking of rheogram for 3-4 h after the establishment of the required temperature (Fig. 135). In this case, the equilibrium modulus, calculated as $E = \frac{P}{\epsilon_m}$, is not invariant at different values of P, i.e., it is not the constant of the time/temporary elasticity of system.

The dependence of equilibrium modulus E on P (Fig. 136) was calculated from with experimental curved $\epsilon = \varphi(\tau)_p$, taken at the temperatures indicated and shear stresses. From curve $\epsilon = \varphi(\tau)$, of emergence and decrease in the deformation (Fig. 137), obtained the method of fractional loads - unloadings it is apparent that both the direct/straight and back stroke by this curve it is nonuniform for the equal portion/fractions of load, which will agree with the data on the dependence of elasticity modulus on shear stress.

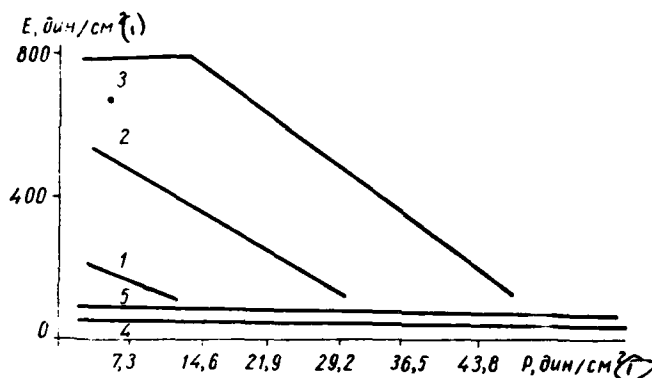


Fig. 136. Dependence of the equilibrium modulus on shear stress for polyether/polyester 1 at temperatures 20 (1), 30 (2), 50 (3), 60°C (4) for unsteady state and 50°C (5) after the achievement of equilibrium.

Key: (1). dyn/cm².

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Temperature of 50°C can be counted for this oligomer of critical, since with its further increase (to 60°C) elasticity modulus does not increase, the strain susceptibility of system sharply is increased (see Fig. 135b, curve 4), but the equilibrium modulus becomes invariant with different shear stresses (Fig. 136, curve 4).

The described state not is stable, and the prolonged holding of

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system at the assigned temperature is accompanied by a change in the strain susceptibility of system with the achievement of the state of equilibrium through the specific time interval (Fig. 138).

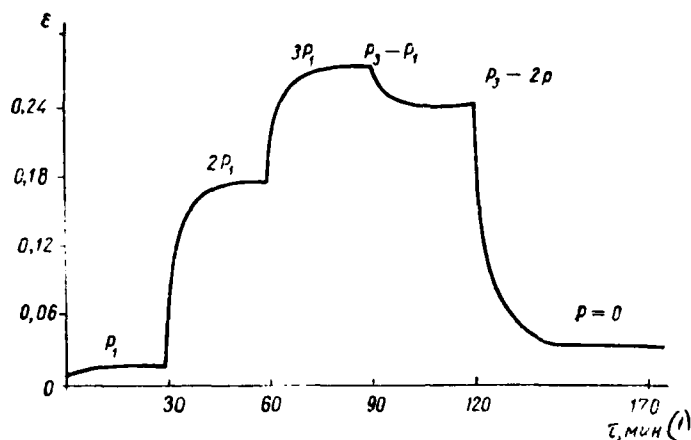


Fig. 137. Dependence of kinetics of the development of shearing strain for polyether/polyester 1 under the condition of fractional loads ($P_1 = 14.6 \text{ dyn/cm}^2$) at temperature of 50°C for unsteady state.

Key: (1). min.

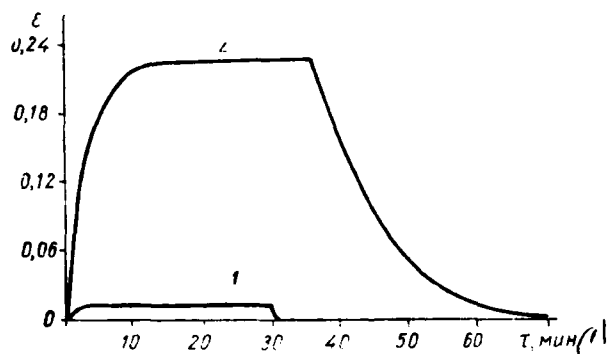


Fig. 138. Change of strain susceptibility of polyether/polyester 1 in equilibrium establishment with 50°C and $P = 14.60 \text{ dyn/cm}^2$: 1 - heating time to 150 h; 2 - heating time are more than 200 h.

Key: (1). min.

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Table 65 depicts the appropriate values of equilibrium modulus E , calculated from curves $\varepsilon = \varphi(\tau)_p$ with different shear stresses (from 7.3 to 43.8 dyn/cm²) and of time of heating (from 30 to 400 h) for temperature of 50°C.

The temperature dependence of kinetics of the development of shearing strain (Fig. 139) was investigated also under conditions of achieving the state of equilibrium at each assigned temperature, in contrast to data of Fig. 135, where curves $\varepsilon = \varphi(\tau)_p$ were remove/taken immediately after the establishment of the corresponding temperature.

Thus, the investigation of the elastic properties of the viscous flow oligomer made it possible to establish that the oligomeric liquids are thixotropic-structured systems, in which is possible the development of the elastic reversible deformations. These data and results of studying the properties of the monomolecular layers of

oligomers [140] and of properties of dilute solutions [97] make it possible to consider that the oligomeric molecules possess their own flexibility and capacity and to changes in the form under the action/effect of voltage/stresses.

The dependence of the value of module/modulus from the voltage/stress (see Fig. 136) can be interpreted as the result of existence in the oligomer of fluctuation amorphous grid/network with the intermittent contacts, caused by the presence of unitary or multiple van der Waals reactions [144]. An incidence/drop of modulus with an increase in the voltage/stress is typical for the structured systems and it is bonded with the thixotropic decomposition of fluctuation grid under the action of shear stresses.

At temperature of 60°C or under conditions of prolonged holding at the lower temperatures when maximally disintegrate or are loosened fluctuation structures, to the foreground project/emerge the deformation properties of the pliable molecules of oligomer, which is developed in distinct emergence and subsequent decrease after to unloading elastic time/temporary strain. In this case the viscous flow polyether/polyester according to the flow properties is such/similar to the stagnant specimen/sample of the elastomer, deformed by the loads, not calling plastic flow of specimen/sample.

Table 65. Dependence of shear modulus on voltage/stress.

U, V	(1) E (дин.см ²) при напряжениях, дин.см ²				
	7,3	14,6	29,2	36,5	43,8
30	610	810	—	—	—
60	6090	2030	277	320	259,0
80	—	2440	286	289	—
150	—	2440	216	—	159,0
200	47,2	68,0	129	—	135,0
400	58,6	95,2	103	87	97,5

Key: (1). E (dyn/cm²) with voltage/stresses, dyn/cm².

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However, oligomers have other specific properties, which are of great interest for understanding of structure it is polyurethane.

During the analysis of the viscoelastic behavior of 100-30o/o solutions of desmophen, were observed the same effects, as for pure/clean oligomers. Elastic properties completely disappeared only with the concentration of solution of less than 30o/o. Consequently, the elastic properties of oligomers and their capability for the formation of grid are developed also in solutions. This indicates the new type of the structure-forming systems to by short polymeric molecules, the occupying the intermediate position between by concentrated solutions and jellies polymers, on one hand, and capable of structurization by colloid solutions of low-molecular substances,

on the other hand. The existence of such structures in oligomers it is very importantly for understanding of properties polyurethane on their basis.

It is necessary, however, to keep in mind that in low-molecular systems the effects of intermolecular interaction are caused also by the presence of polar end groups, moreover this factor will manifest itself greater, the lower molecular weight of oligomer, which follows from the thermodynamic analyses of the solutions of the properties of monomolecular layers [140, 179].

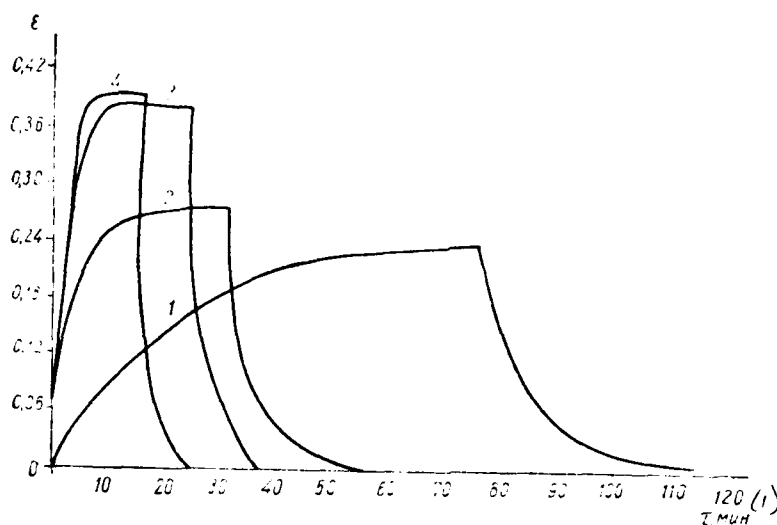


Fig. 139. The dependence of kinetics of the development of shearing strain for polyether/polyester 1 at different temperatures for the state of equilibrium: 1 - 30; 2 - 50; 3 - 60; 4 - 70°C.

Key: (1). min.

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It is established/installed, that between the molecules of oligomers there are significant cohesive forces and that during the compression of the monomolecular layers of oligomers occur the processes, bonded with the flexibility of oligomeric chains and the decrease of the aggregates of oligomer molecules [140]. The processes of aggregation in the solutions of polyethylene glycols are

described in works [168, 205].

Findings indicate the need for the account the anomalies of the flow properties of oligomers during processing/treatment and obtaining of them of polymeric materials. As the interesting illustration of this position can serve following phenomenon [118]. The effect of anti-thixtropy was used during obtaining of three-dimensional grids in the course of their synthesis under conditions of act/effecting the shift voltage/stresses for 80-120°C. Three-dimensional and linear polyurethane are obtained on the basis of diethyleneglycoladipate and polyfurite directly in rheoviscosimeter with the rotation of jacket prior to the beginning of gel formation and at shearing rates 0.07 and 0.04 s⁻¹. Figure 140 gives the curve of the dependence of ductility/toughness/viscosity on the shearing rate for blocked macro-diisocyanate, on the basis of which are selected those shearing rates, by which is observed the increase of ductility/toughness/viscosity. Table 66 gives data on the mechanical properties of those obtained it is polyurethane whose three-dimensional/space grid is formed by chemical and physical bonds, and also for a comparison the data on the properties of the same system, synthesized under normal conditions.

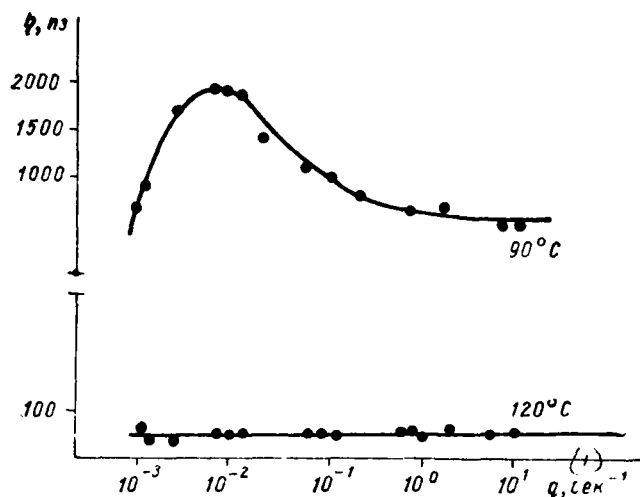


Fig. 140. Dependence of the ductility/toughness/viscosity of model system on the velocity gradient.

Key: (1). s^{-1} .

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As is evident, is observed the significant anisotropy of mechanical properties in flow direction and it is perpendicular to it. This anisotropy is not developed, at the synthesis of news with the higher velocity gradients, which correspond to the descending branch to curved Fig. 140. This indicates that as a result of the orientation of oligomeric molecules in the field of shift voltage/stresses shaping of cross connections (chemical and physical) occurs

predominantly in the direction, perpendicular to the axis of the molecule where the probability of the formation of such bonds is more than in the direction of flow. This effect leads to the anisotropy of the obtained grid.

ADHESION OF POLYURETHANES TO RIGID SURFACES.

Polyurethane widely are used as glues, and also for the coating of wood/tree, metals, paper, clothes, glass, skin [11, 55, 126, 171, 180, 194, 199, 201, 248, 320-322, 336, 340]. Polyurethane coatings possess a good adhesion to different surfaces, light- and are resistant to atmosphere, they retain well gloss, they possess good electrical properties and low gas permeability, and it is also resistant to the action/effect of solvents. Glues are used for the cementing of glass, wood/tree, plastics, rubbers, polyethylene, wool, fibers, metals, skin [80, 223, 232, 241, 261, 277, 278, 288, 315, 316].

In connection with large practical application/use it is polyurethane it appears the need for the investigation of the processes, which occur with the formation of polyurethane film on surface, effect on these processes of nature and relationship/ratio of the components, which compose coating, temperatures, presences of the additions and some other factors. In this direction known only several works, which concern the investigation of adhesion are polyurethane to rigid surface [133, 291, 292].

Table 66. Tensile strength of the specimen/samples of polymers (kg/cm²), of synthesized in field shift voltage/stresses.

(1) Состав композиции	(2) Градиент скорости сдвига. сек ⁻¹		
	0	0,7381	0,0715
(3) Олигодиметиленгликольадипинат-2050: Т-65: сшиватель = 1:1,15:0,08	6,82 ↑		20,7 *
(4) Олигофурит-1680: 2,4 - ТДИ: МОСА = 1:1:1	6,82 →		10,7 *
	76,0 ↑	133,0 ↑	177,0 *
	76,0 →	181,0 *	105,0 →

Note. Rifleman/pointers showed the direction of cuttings of specimen/samples made of polymer (↑ along the axis of cylinders, → along flow).

Key: (1). Composition of composition. (2). Gradient of shearing rate s⁻¹. (3). Oligodimethyleneglycoladipinate-2050: Т-65: cross-link. (4). Oligofurite.

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Is studied the adhesion of polyurethane coatings on the basis polyethers depending on the structure of latter and nature of the fillers, introduced into films, by the method of the breakaway of film from aluminum base at angle of 180°, but sometimes 90° for the film of different thickness. The dependence of the value of adhesion from thickness was straight lines whose slope/inclinations, according

to [292, 293], were bonded with the hardness of the film: the greater the slope/inclination, the greater the hardness. Extrapolation of straight lines to zero thickness gave the values, which were the characteristics of the adhesion of the investigated materials.

For studying the dependence of adhesion on the structure of polyol used it is obtained film on the basis of polypropylene glycol (series P), polyoxypropylene derivative of trimethylol propane (series TP) and polyoxypropylene derivative of glycerin (series GP). All glycols and polyol had different molecular weight. Films broke away under two angles with speed of breakaway 0.25 cm/s.

As can be seen from Fig. 141, the greatest adhesion have coatings on the basis of polypropylene glycol P-410, smallest - on basis TP-740. The value of adhesion is more with breakaway at angle of 90°. During the comparison of data according to adhesion and mechanical characteristics, it turned out that the films have with high adhesion great ultimate elongation and the smallest module/modulus during 100% elongation. The author [292, 293] comes to the conclusion that the films on basis P-410, having the smallest hardness, more easily are adapted to rigid surface and due to this adhesion grow/increases. The application/use of the branched polyol leads to the formation of grid thicker and, therefore, with the greater hardness of the cuts or chains, which decreases the adhesion

(see Fig. 141).

The utilization of stereoregular polypropyleneglycol considerably increases adhesion [293] in comparison with the atactic of the same molecular weight. Reason can be the tendency of isotactic polymers to be crystallized in winding structures.

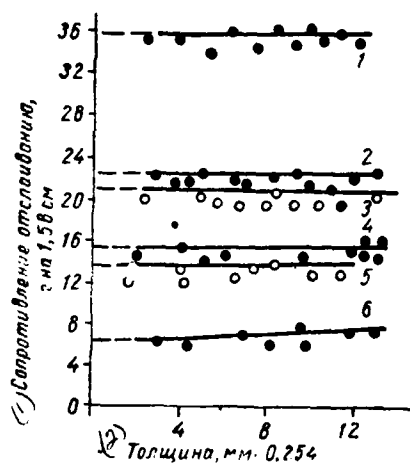


Fig. 141. Dependence of the adhesion of polyurethane films on the nature of polyether/polyester and angle of the breakaway:

1 — 90°, П-410; 2 — 180°, П-410; 3 — 90°, П-410; ТР-740; 4 — 180°, П-410; ТР-740; 5 — 90°, ТП-740; 6 — 180°, ТП-740.

Key: (1). Resistance to stratification, 2 on 1.58 cm.

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In this case polar groups can be located on the external surfaces of such spirals and therefore are created possibilities for forming a large quantity of van der Waals and hydrogen bonds with oxide film on the surface of aluminum.

A similar effect was observed for polymethyl methacrylate [222, 272]. The polyol, which contain fluorine, decrease adhesion, in spite

of small differences in the hardness of films on the basis of the fluorine-bearing polyol and generally accepted polyol.

Is investigated the effect of the nature of diisocyanate on the adhesion of coatings on the basis of xylylenediisocyanate, TDI and diphenylmethanediisocyanate [293] and is establish/installed, that coating on the basis of diphenylmethane diisocyanate, in spite of their high hardness, they possess the greatest adhesion to aluminum base. Explanation to this effect the authors do not give.

The investigation of the dependence of adhesion on the relationship/ratio of NCO/OH--group on the coatings, obtained on the basis of polyol TP-700 with different content of TDI showed [294] that with increase of the relationship/ratio of NCO/OH--group the adhesion decreases, but increases module/modulus with 100o/o elongation and tensile strength. The decrease of adhesion with an increase in relationship/ratio NCO/OH and, consequently, also network density it is joined with an increase in the hardness of polyurethane films.

On the other hand, it is reveal/detected that an increase in the content of urethane ones and, especially, uric groups leads to an increase in the adhesion, in spite of the increase of the density of cross-linking.

For the establishment of effect on adhesion, it is polyurethane both of factors is simultaneously studied the adhesion of films on the basis of glycols and branched polyol of different molecular weight. An increase in molecular weight poly-ode gives and to the decrease of the maintenance of urethane groups and network density simultaneously. The same dependence is obtained for glycols (Fig. 142) and branched polyol. According to [292], in this case an increase of the adhesion as a result of an increase in the content of urethane groups is considerably covered with its lowering because of the increase of the hardness of film, caused by an increase in the density of cross-linking. If this then, then adhesion will achieve maximum value with some average/mean content of urethane groups, which ensures the optimal elasticity of film.

During obtaining of polyurethane coatings, are used different in their nature solvents.

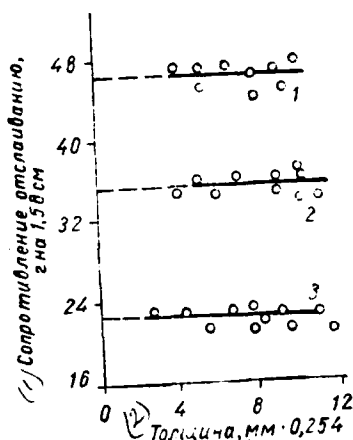


Fig. 142. The effect of molecular weight of glycol on the adhesion: 1 - P-2010; 2 - P-1310; 3 - P-410.

Key: (1). Resistance to stratification, g on 1.58 cm. (2). Thickness, mm 0.254.

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It is known that depending on the thermodynamic quality of the solvent of the molecule of polymers they have different conformation in solution. The degree of the contacting of polymer chain with rigid surface depends on form of the chain and, consequently, also the nature of solvent. All this must affect the value of the adhesion of polymer network, in this case of polyurethane, to rigid surface.

The effect of the solvent, utilized for obtaining the varnish, on adhesion is investigated in work [293]. Polyurethane coatings were obtained on the basis of polypropylene glycol, trimethylol propane and TDI. As can be seen from the dependence of the value of adhesion from the nature of the solvent (Fig. 143) used, the greatest adhesion possess the films, obtained with the utilization of cyclohexanone, smallest - with the application/use of xylene. The author joins this with a change in the energy density of the cohesion of solvent. But for cyclohexanone, dioxane and acetone the energy density of cohesion is identical, but adhesion is different, consequently, this explanation is unacceptable.

One of the reasons for the dependence of adhesion on the nature of solvent, according to [293], different rate of evaporation of solvent during the solidification of coating. It seems to us by most correct this explanation the effect of the nature of solvent on adhesion, which considers the dependence of chain conformation on the nature of solvent.

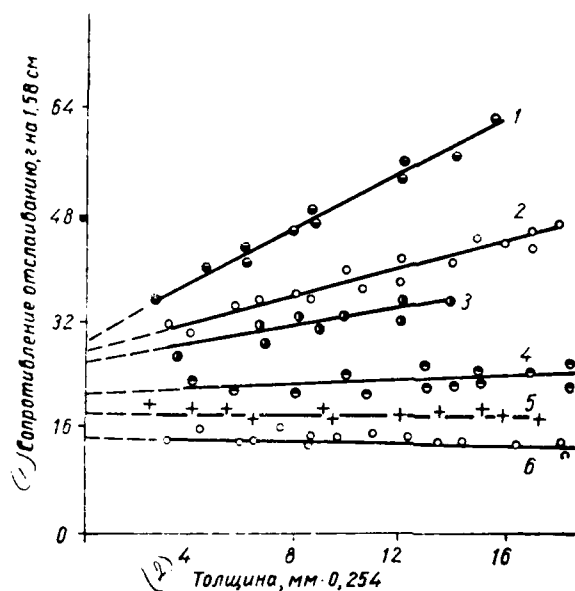


Fig. 143. The dependence of adhesion on the nature of the solvent: 1 - cyclohexanone; 2 - dioxane; 3 - acetone; 4 - chloroform; 5 - benzene; 6 - xylene.

Key: (1). Resistance to stratification, g on 1.58 cm. (2). Thickness, mm $\cdot 0.254$.

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It is known that in a good solvent the polymer chains are more unwound and, therefore, is provided to greater degree their contact with surface. After the vaporization of solvent, one should expect large adhesion. In the poor solvents (chloroform, xylene and benzene)

of molecule, they are displaced, which impedes their contact with surface and decreases the adhesion.

During the analysis of the adhesion of polyurethane coatings there is a definite interest in the dependence of adhesion on nature and concentration of fillers and addition, introduced into films is polyurethane. Study of the effect of some fillers for the adhesion of polyurethane coatings to aluminum [292] showed that the introduction to dioxide of titanium decreases the adhesion of coatings by basis POPG-1300, polyoxypropylene derived trimethylol propane and TDI to 15o/o, but talc - to 40o/o. The dependence of the value of the adhesion of film on basis P-2010, TP-1540 and TDTs from the nature of other fillers is represented in Fig. 144, from which is evident slope deviation of the direct dependence of adhesion on the thickness of film. The author explains this by the fact that the film becomes harder with the introduction of the filler on nature of which depends the slope/inclination. Introduction ZnO and CaCO₃ leads to an increase in the adhesion in contrast to TiO₂ and of talc. An increase in the adhesion was observed also with an increase in the adhesion not symbatically with an increase in the concentration of such fillers as Fe₂O₃ and CaCO₃ (Fig. 145). A maximum increase in the adhesion is observed with the optimal content of filler. For Fe₂O₃ and CaCO₃ this value is 15 vol.o/o. An increase in the content of oxide of chromium in film leads to monotonic lowering in the

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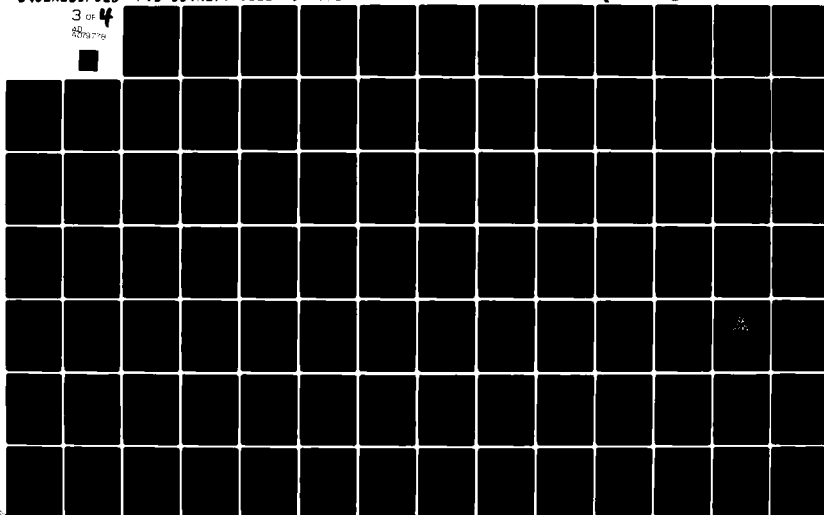
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adhesion.

The effect of fillers on the value of adhesion according to [292] depends on the particle shape of the filler. The author also assumes that the fillers are capable of changing the wettability of polyurethane coatings with respect to metal, although no experimental data on this question are given.

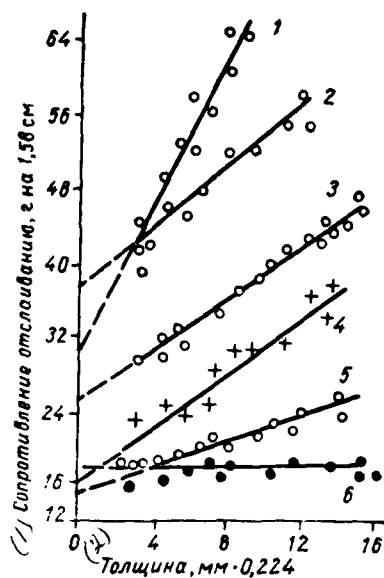


Fig. 144. The dependence of adhesion on the nature of the fillers: 1 - ZnO ; 2 - CaCO_3 ; 3 - CaCO_3 cubic form; 4 - TiO_2 ; 5 - BaSO_4 ; 6 - without filler.

Key: (1). Resistance to stratification, g on 1.58 cm. (2). Thickness, mm=0.224.

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The effect of fillers on adhesion in this case can be explained, on the basis of different reaction of fillers with polymer chains or, it is more accurate, with the cuts of the polymer chains between nodes,

the which changes structure polymer. Furthermore, it is necessary to consider the effect of different nature of fillers on the course of reactions during the formation of polyurethane coatings, which also is reflected in the structure of film and, consequently, also in its adhesion to base. Works in this direction, unfortunately, were not conducted.

The adhesion it is polyurethane it affects the structure of metallic base [154], in particular the state of crystalline structure of copper. The study of the adhesion of polyurethane coatings (varnish UR-930 and varnish on the basis of adduct KT) to the surfaces of the cold-rolled and electrolytic copper foil showed that the adhesion to the cold-rolled foil is much higher than to electrolytic.

Roentgenographic investigation of both of forms of the copper foil showed difference in the state of crystal structure of copper. This, possibly, and conditioned sharp difference in adhesion was polyurethane to the surface of the cold-rolled and electrolytic copper foil.

As is known, polyurethane compositions are used as glues. The strength of cementing affect the same factors, as for the adhesion of polyurethane coatings: the nature of polyether/polyester,

poly-isocyanate, etc. In work [308] is explained the effect of hydroxyl number of polyether/polyester and the addition of different joints on the strength of gluing of duralumin of polyurethane composition on the basis of "Desmodur TN" (2.4-TDI+trimethylolpropane) and "Desmophen-800". showed that with the decrease of the hydroxyl number of "Desmophen-800" is increased the strength of cementing, which is characterized by the value of shearing strength.

Introduction to the polyurethane composition of different additions led both to an increase and to the decrease of shearing strength in dependence on the nature of addition. So, the addition of aliphatic glycols considerably decreased the shearing strength.

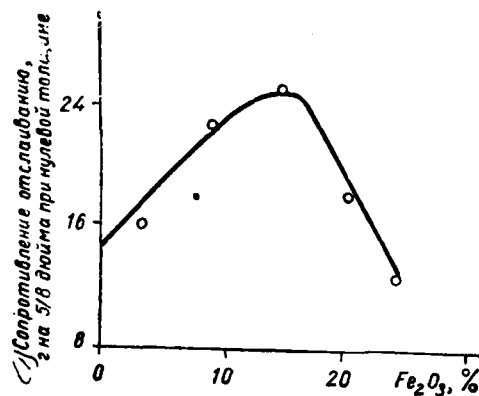


Fig. 145. The effect of content Fe_2O_3 on adhesion it is polyurethane.

Key: (1). Resistance to scaling, g to 5/8 inches with zero thickness.

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Inverse effect is reached during the addition to polyurethane of mono- and dioxybenzene, dimethylhydroxybenzene and especially methyl and phenyl-substituted of ethoxysilane. The influence of additions on the strength of cementing the authors explain by the catalytic action of some of them.

The study of the dependence of the strength of the cementing of duralumin by polyurethane on temperature showed that with an increase in the temperature, at which is conducted the cementing, is increased

shearing strength, reaching the maximum value with 130°C. The investigated bonds are unstable to the action/effect of many organic solvents and water. So, in acetone the strength of bond falls on 100, in benzene - to 70, m-cresole and water - to 60, also, in gasoline - to 70/o. These results are contradictory to the data, which relate to the adhesive strength of expanded polyurethane to the metals and its dependence on temperature and action/effect of water [133].

Thus, application/use of polyurethane compositions as coatings and glues gives good results and depends on a number of factors. Primary meaning has a presence of polar urethane groups. This conclusion/derivation asserts itself in the examination of the investigations, which concern an improvement in the adhesion of synthetic and natural rubbers to metal and wood during the addition to them of isocyanates [253]. Good results are obtained during the treatment of the cemented object/subjects (from metal and wood) triisocyanate and by the subsequent deposition of glue from rubber. The adhesion of some polymers to different surfaces is improved with their mixing with poly-isocyanates [251, 299, 309], especially with the optimal impurity/admixture of triisocyanate. It is obvious, isocyanate groups in a small quantity form the insufficient concentration of the bonds between surface and glue, but, on the other hand, the application/use of large quantities of isocyanate hardens composition, decreases the flexibility of polymer chains and

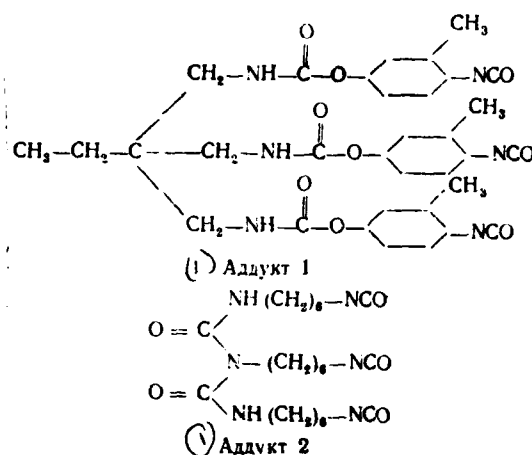
thereby impairs the adaptability of the latter to rigid surface. Therefore the best results on adhesion will be always observed with some optimal content of isocyanate, used as impurity/admixture to other glues [253] and polyurethane compositions.

Survey/coverage of works on the adhesion of polyurethane coatings and glues bears surface character. In the examination of the effect of components (polyether/polyester, diisocyanate, concentration of different groups) on adhesion not in one case was studied the effect of these components to structure was polyurethane. Meanwhile the structure of three-dimensional grid, which appears during solidification it is polyurethane on rigid surface and defined as by the nature of components it is polyurethane, so also nature of the rigid surface, on which occurs the formation of coating, it is the basic factor, which are determining adhesion. Therefore during the investigation of the adhesion of polyurethane coatings to different surfaces, one should approach/fit this question from the point of view of the dependence of adhesion on the structure of three-dimensional grid. It is, first of all, necessary to investigate the effect of rigid surface on the structure of three-dimensional grid.

Surface has noticeable effect on the character of the forming grid as a result of the fact that the cuts of the chains between chemical network points, possessing noticeable flexibility, are capable of being adapted to surface and of interacting with it. In this case, are formed the additional physical bonds polymer - base whose concentration depends on nature and relationship/ratio of components.

For investigation of a change in the structure of grid, it is polyurethane in the presence of rigid surface was studied the effective density of films, which were being located on base, and the free films, obtained under the analogous conditions of solidification [67, 116]. As the subjects of investigation served polyurethane coatings on the basis of the copolymer tetrahydrofurane with 25o/o of oxide of propylene (TGF - 25o/o of OP) of the different molecular weight of oligodiethyleneglycoladipate (ODA), oligodiethyleneglycolsebacate (ODS), and also of silicon-bearing polyol. As isocyanate component were taken the adduct of trimethylol propane from TDI (adduct 1) and polyisocyanate of biuret structure (adduct 2).

Simplified formulas of adducts following:



Key: (1). Adduct.

Free films of polyurethane are obtained by casting the composition on Teflon or glass, pre-processed so as to bring together the adhesion of film to surface to minimum. For determining the network density in the presence of the rigid surface of coating, they are brought in to aluminum foil with a thickness of 14 μ . The value of the effective density of cross-linking is characterized by the value of average molecular weight between network points M_c .

Are obtained dependences M_c of free films and films on the basis of polyurethane coatings on the basis of TGF - 250/o OP on molecular weight of initial polyether/polyester during relationship/ratio $\text{NCO}/\text{OH}=3:1$ (Fig. 146), and also on the relationship/ratio of NCO/OH -group with molecular weight of polyether/polyester indicated

above, equal to 1000 (Fig. 147).

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Network density on base is always more (less M_c) than free films, which indicates the emergence of additional, physical bonds the polymer - base. With an increase in molecular weight of initial polyether/polyester (see Fig. 14b) with one and the same relationship/ratio NCO/OH by the decrease of the content of NCO--group per unit of volume and, therefore, with the decrease of a number of the molecular bonds, caused by the interaction of the polar groups with each other and with base. With an increase in relationship/ratio NCO/OH, is increased the effective density of cross-linking, which is completely regular, but furthermore decreases the difference between M_c free film and film on base. During relationship/ratio NCO/OH=4:1 in both cases M_c virtually it is equal. It is obvious, during the smaller relationship/ratios NCO/OH (with a smaller quantity of introduced chemical network points) the adaptability of the cuts of the chains between nodes to rigid surface is more than during the large relationship/ratios NCO/OH, when the presence of the excess of NCO--group contributes to rigidity of chains, as a result of the course of secondary reactions with the formation of allophanate and biuret bonds. Therefore with smaller NCO/OH is possible the formation of a greater quantity of bonds

polymer - base.

The decrease of a difference between M_c in the free film and film on base occurs, also, during introduction to polyurethane composition on the basis of TGF - 25o/o of OP of the additional structuring agent - trimethylol propane (table 67). The difference between M_c free film and plate/bar on base decreases with an increase in the quantity of introduced trimethylol propane.

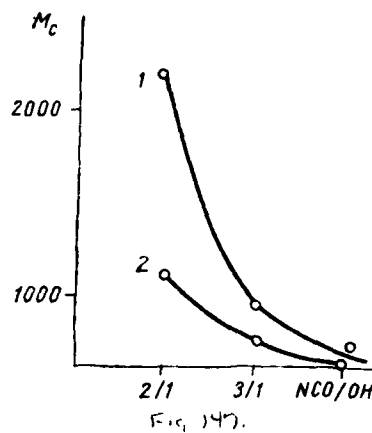
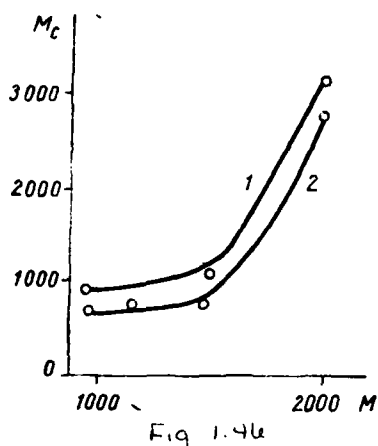


Fig. 146. Dependence M_c of films on the basis of TGF - 250/o OP on molecular weight of polyether/polyester: 1 - free film; 2 - film on base layer.

Fig. 147. Dependence M_c of films on basis of TGF - 250/o of OP-1000 on relationship/ratio NCO/OH: 1 - free film; 2 - film on base.

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Somewhat different affects the effect of base the network density of polyurethane films on the basis complex oligoesterglycol. The introduction of the latter to grid must give in to an increase in the number of intermolecular physical bonds due to the presence of the carbonyl group, capable of reaction with the urethane groups through hydrogen bonds.

Dependence M_c of films on the relationship/ratio of NCO/OH--group for it is polyurethane on basis of ODA of different molecular weight (Fig. 148) shows that for polyurethane on basis of ODA of molecular weight 600 the network density of free film is more than on base.

During an increase in molecular weight of ODA to 800 effective density of the cross-linking of free film decreases, which is regular, but value M_c of free films and films on base identical. This is bonded, obviously, with the fact that the stronger the interaction with the surface of initial oligomers changes shaping

conditions for grid.

On one hand, with shaping of film on the surface, it is sufficient strongly with it which interacts, occurs the formation of physical bonds polymer - surface, that contribute the specific contribution to overall network density. On the other hand, the reaction of oligomers and growing chains with surface leads to the limitation of their mobility. In this case, is possible the deactivation of reaction centers and the increase of the velocity of the break of reaction chains on surface, as a result of which the denseness of the generating grid decreases and the latter will become more defective. The presence of defects in grid logically depends to a considerable extent on the flexibility of units in polyurethane. So, with smaller molecular weight of oligoester the flexibility of the chain between nodes in grid decreases and should expect the greater defectiveness of grid. Therefore network density in film on base can prove to be less than in free film, that also is observed.

Table 67. The effect of the addition of trimethylol propane on the effective density of cross-linking in polyurethane on the basis of the copolymer of tetrahydrofuran with 25% of propylene oxide.

ТМП, %	M_c сво-бодной пленки	M_c пленки на подлож-ке (2) кс
0	2230	1100
25	600	460
50	450	300

Key: (1). free film. (2). film on base.

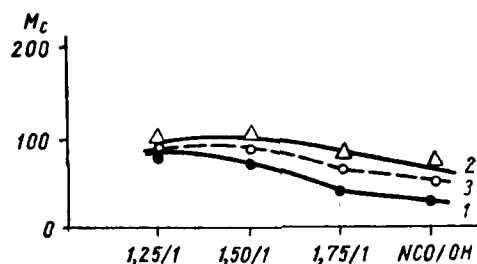


Fig. 148, dependence M_c of films on basis of ODA on relationship/ratio NCO/OH: 1 - free film on ODA (mol. weight 600); 2 - film on base (mol. weight 600); 3 - film on base and free film on ODA (mol. weight 800).

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An increase in molecular weight of oligoester raises the flexibility of the cuts of chains, increasing their mobility and even when to the

decrease of the defectiveness of grid. In this case, is increased a number of bonds polymer - base as a result of the best adaptability of more flexible chains to rigid surface. Under specific conditions it is possible that the effective density of cross-linking on base can become equal to the same for a free film, that also is observed for it is polyurethane on basis of ODA of molecular weight 800. During further increase in molecular weight of oligoester, it can seem that M_c on base will become less than M_c free film, i.e., will be observed the phenomenon, analogous examined for simple oligoester.

It is interesting to trace the effect of the nature of complex oligoester with identical molecular weight on the network density of the formed on their basis polyurethane films. Is establish/installed dependence M_c on the relationship/ratio of NCO/OH--group for polyurethane coatings on the basis of ODS (Fig. 149). The analysis of Fig. 148 and 149 shows that with one and the same molecular weight of oligoester the effective density of cross-linking for ODA is more than for ODS. Replacement of ODA by ODS leads to the decrease of the content of carbonyl groups per unit of volume and, therefore, to the decrease of the concentration of secondary bonds, which affects the common/general/total network density. In the case of the smaller relationship/ratio of NCO/OH--group, the effective density of cross-linking on base is considerably more than free film, which will agree with above-stated presentation/concepts.

The study of the effect of aluminum base on the effective density of the cross-linking or coatings on the basis of glycoxysilanes showed [78] that the network density is determined by the structure of glycoxysilane, by its degree of branching. At the same time it is revealed/detected that after the solidification of coatings the denseness of their grid in the presence of rigid surface is changed during long time (Fig. 150). M_c free films do not depend on time, while M_c films on base somewhat decreases. Probably, in the presence of rigid surface, shaping of grid continues slowly, that also is characterized by prolonged change M_c in time. Is possible also the redistribution of bonds in the course of time in quite polymer film.

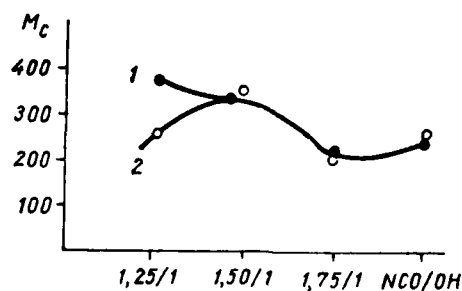


Fig. 149. Dependence M_c of coatings on the basis of ODS (mol. weight 600) on relationship/ratio NCO/OH: 1 - free film; 2 - film on base.

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For the investigation of the dependence of the effective density of cross-linking on the nature of poly-isocyanate, are obtained the films on the basis of tetradiehtyleneglycoxysilane with the utilization of adducts 1 and 2. It is shown, that absolute values

M_c of films on the basis of adduct 1 are more than on the basis of adduct 2. This is bonded with the smaller content of NCO-group per unit of volume in the first case. On the other hand, if in films on the basis of adduct 1 M_c on base it is more than free films, then in coatings on the basis of adduct 2 is observed reverse picture. It is possible, the presence in the molecule of the adduct of 2 methylene groups leads to the formation of the more pliable cuts of chains in three-dimensional/space grid, what provides a greater quantity of

bonds polymer - base. The presence of aromatic groups in adduct 1 contributes to greater rigidity of chains in grid, what decreases the possibility of the formation of bonds polymer - base conditions the formation of more defective grid.

Thus, the effective density or the cross-linking of polyurethane coatings in the presence of base is determined by the nature of oligoester, by its molecular weight, nature of utilized isocyanate and by relationship/ratio of NCO/OH--group. The factors indicated affect the flexibility of chains it is polyurethane, determining thereby the relationship/ratio of physical and chemical nodes in grid.

With the formation of grid on surface one should consider the simultaneous course of two processes: the formation of the physical bonds polymer - rigid surface, which must increase network density; the limitation of the mobility of growing chains as a result of their reaction with rigid surface, which leads to the formation of the more defective grid, which is characterized by a smaller number of nodes, than such of free film.

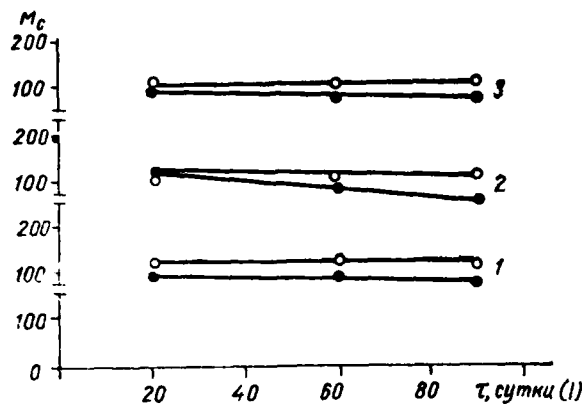


Fig. 150. Change M_c in time for polyurethane coatings on the basis of dimethyldibutylene glycoxysilane during different relationship/ratio NCO/OH: 1 - 1.5:1; 2 - 1.75:1; 3 - 2.00:1 (○ - free film; ● - film on base).

Key: (1). days.

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In the case of the prevalence of the first process above the second, we obtain M_c the film, formed in the presence of rigid surface smaller than free film, which occurred for coatings on the basis of simple oligoester. The increase of rigidity of chains because of an increase in relationship/ratio NCO/OH and in introduction of oligoester units with the groups, capable of reaction with urethane

ones (for example, ester units), contributes to the course of the second process, i.e., to the formation of more defective grid conditions increase M_c of the film in the presence of base in comparison with free film.

A change in the structure of film under the effect of rigid surface affects its adhesion. By us is studied the dependence of adhesion it is polyurethane on the network density and nature of base [79] and it is made the attempt to determine the value of adhesion which does not depend on the secondary factors: the thickness of coating, velocity of its stratification and in connection with this electrostatic phenomena [3].

Is investigated the adhesion of coatings on the basis of TGF - 250/o of OP of molecular weight 1200 and of adduct 1 to aluminum, brass, steel and glass bases [79]. Energy of adhesion is determined on the adhesion meter AZS-2 [51], in which was changed strength measuring part and the place of strengthening testing roller is located on dynamometer. The coating being investigated will be brought in from solution to testing roller during its rotation and is solidified at temperature of 80°C. Testing rollers were made from metal and glass and they have free running because of which the angle of breakaway always remains constant and equal to 90°. The position of the boundary/interface of breakaway also is constant relative to

the stratifying effort/force. During testing the edge of the strip of the coating being investigated they reinforce in the clamp, which was being moved with given speed which can be changed within the limits of 0.025-0.3 cm/s.

During testing with given speed of stratification, occurs a smooth increase in the fixed/recorded effort/force (Fig. 151^{AB}), and then the effort/force or breakaway remains almost constant (Fig. 151^{BC}). This effort/force corresponds to the voltage/stress of stratification in known unstuck speed (P_1). From the averaged stress level with breakaway, is determined the energy of adhesion of coating at the given velocity of stratification, in reference to the unit of the width of film.

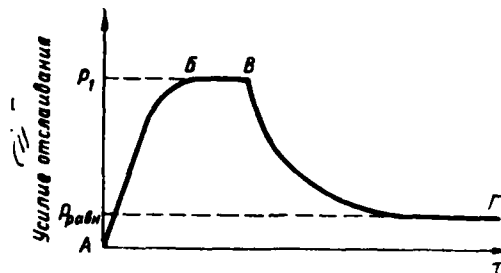


Fig. 151. Change in the effort/force of stratification in time at given speed of stratification.

Key: (1). Effort/force of stratification.

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If we after the determination of the effort/force of breakaway with the known velocity of stratification stop the displacement/movement of clamp, then the stratification of film it is continued as a result of relaxation of the voltage/stresses in the film, which leads to abbreviation for the latter. Stratification occurs to those pores, while the voltage/stresses in film will not be equalized by the forces of interaction of the coating being investigated with the surface of roller - adhesive forces (Fig. 151^{CD}), after which the stratification ceases (Fig. 151, point D). The value of residual voltage/stress, in reference to the unit of the

width of film, the authors call quasi-equilibrium energy of adhesion. Figure 152 gives typical the curves of stress relaxation in films, from which are calculated the values of quasi-equilibrium energy of adhesion (Table 68).

Energy of adhesion diminishes in series/number steel > brass > dural > glass, also, during an increase in the network density (increase NCO/OH, decrease M_c) grow/increases in all cases.

Introduction to coatings and glues of the compounds, which contain isocyanate groups, usually leads to an increase in adhesion [251, 299, 309]. Therefore, the increase of adhesion with growth NCO/OH and, consequently, also network density it is logical result. For clarity is represented the dependence of energy of adhesion on network density (Fig. 153). For coatings with greater network density, is observed critical dependence of adhesion on the nature of base despite the fact that a change in the network density during a change in the type of rigid surface is small. It is possible that sharp increase in the adhesion with a change in the nature of surface can be explained by different reaction of bases with the investigated coatings due to the dissimilar character of the joining of functional groups, which are located on the surface of metals, with polyurethane.

Table 68. Dependence of the energy of adhesion ($A \cdot 10^{-5}$ erg/cm²) of polyurethane coatings on the nature of base, network density and unstick speed.

(2) Подложка	NCO/OH = 2 : 1					NCO/OH = 4 : 1					(1) NCO/OH = 2 : 1 с добавкой 50% ТМП				
	(3) А при скорости отрыва, см/сек			(4) Равновесная работа адгезии, эрг/см²	M _c	(3) А при скорости отрыва, см/сек			(4) Равновесная работа адгезии, эрг/см²	M _c	(3) А при скорости отрыва, см/сек			(4) Равновесная работа адгезии, эрг/см²	M _c
	0,3	0,1	0,025			0,3	0,1	0,025			0,3	0,1	0,025		
Сталь (5)	4,70	3,70	2,90	0,47	—	6,90	6,00	4,80	1,97	—	9,00	7,30	6,00	2,25	—
Латунь (6)	4,50	3,75	2,65	0,34	350	6,50	4,90	4,50	1,50	250	12,50	11,50	7,80	3,92	150
Дюраль (7)	3,30	2,65	2,00	0,34	450	3,15	3,00	2,90	0,75	220	3,50	3,30	3,20	0,67	130
Стекло (8)	2,90	2,90	2,00	0,27	—	2,60	2,45	2,20	0,30	—	2,80	2,60	2,40	0,59	120

Note. Energy of adhesion at unstick speeds 0.025-0.3 cm/s is related to the thickness of 0.11-0.12 mm.

Key: (1). with addition. (2). base. (3). A at unstick speed, cm/s.
 (4). Equilibrium energy of adhesion, erg/cm². (5). Steel. (6). Brass.
 (7). Dural. (8). Glass.

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During the explanation to dependence of adhesion on the nature of base, it is necessary to consider following. It is known that the surface tension of the materials of the bases being investigated diminishes in the same order as the energy of adhesion, determined by us for these bases [129, 273] (Table 69). Substances with large surface tension possess greater surface energy, which, possibly, and

causes stronger interaction of investigated polymers with metals (in particular, with steel), than with glass. The analysis of results Table 69 shows that the energy of adhesion depends on the velocity of stratification. Furthermore, with an increase in the thickness of coating increases energy of adhesion (Fig. 153, curve 1). An increase in the work of breakaway with an increase in the thickness is observed usually during the utilization of a method of stratification [3] and it is especially characteristic for elastic coatings. This phenomenon is bonded with the voltage/stresses, which appear with bend, and also with deformation of film according to thickness with its breakaway from base. The work, spent on the deformation of film, is increased with an increase in the deformation rate and the thickness of film, affecting thereby the work of the breakaway of coating. Thus, for obtaining the comparable results in the capacity of adhesion it is necessary to investigate the coatings of identical thickness with the same velocity of stratification. The procedure of obtaining the films of identical thickness is very complex.

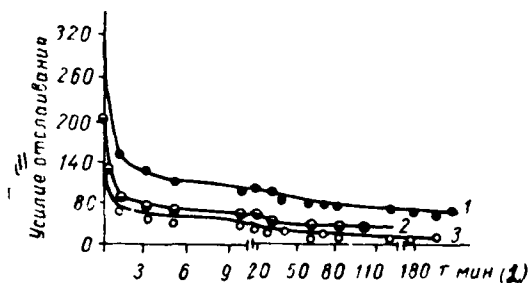


Fig. 152. A change in the effort/force of stratification in time because of the voltage/stresses, which arose in film with its stratification, at a rate of 0.025 cm/s for a coating with relationship/ratio NCO/OH=2:1 and with addition 50o/o TMP: 1 - steel; 2 - dural; 3 - glass.

Key: (1). Effort/force of stratification. (2). min.

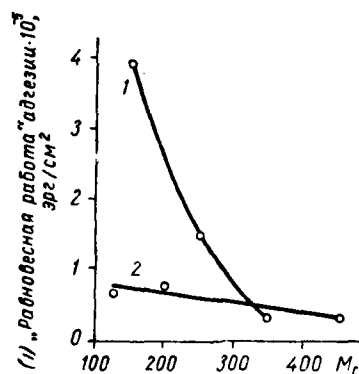


Fig. 153. Dependence of quasi-equilibrium energy of adhesion on network density: 1 - brass; 2 - dural.

Key: (1). "equilibrium work" of adhesion $\cdot 10^{-5}$, erg/cm².

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Furthermore, for evaluating the adhesion of the coatings of one nature, but different network density even the identical thickness of films always can ensure obtaining the comparable results, and since the mechanical properties of these films are not identical, then also the work which proceeds with their deformation with breakaway, it will be different.

The values of quasi-equilibrium energy of adhesion do not depend on the thickness of coatings and initial velocity of breakaway (Fig. 154, Table 70), what is completely regular result, since character and strength of joining polymer - rigid surface is determined by the structure of a comparatively thin layer of polymer, adjacent to surface [64]. Therefore adhesion is determined not by the thickness of coating, but by the nature of base and by the structure of polymer.

In terms of absolute value the value "of equilibrium "energy of adhesion, as can be seen from Table 68, composes 10-40o/o of energy

of adhesion, determined at final unstick speeds, which will agree with conclusion/derivation [91] about the decisive contribution of the work of deformation to the total balance of the work of stratification.

On the basis of the above it is possible to expect that the value of the quasi-equilibrium energy of adhesion during determination of which are remove/taken the effects, bonded with the thickness of coating, its deformation, velocity of stratification and in connection with this electrostatic phenomena, it more correctly characterizes the value of intermolecular interaction on interface, than the determined usually work of peeling polymeric coatings from rigid surface.

It was noted that the rigid surface exerts a substantial influence on the effective density of the cross-linking of cross-linked ones it is polyurethane. It is interesting to explain, at what depth stretches the action/effect of base in the investigated case. For this purpose, is carried out the definition of the effective density of cross-linking both free films (obtained via infusion to film from fluoroplast) and films on the materials of different nature [54]. The thickness of films varies from 10 to 300 μ .

Table 69. Values of the surface tension of some metals and glass.

(1) Вещество	(2) Температура опре- деления, °C	(3) γ, дин/см	(4) Граница раздела
Железо (5)	1267	936	H ₂
(6)	1310	917	H ₂ (7)
Алюминий	700	840	Воздух
	706	494	Пары (8)
Стекло (9)	550	135—170	алюминия (6) Воздух

Key: (1). Substance. (2). Temperature of definition, °C. (3). dyn/cm. (4). Boundary of section. (5). Iron. (6). Aluminum. (7). Air. (8). Vapors of aluminum. (9). Glass.

Table 70. Change in the energy of adhesion with the speed of stratification.

(1) Подложка	(2) Скорость отслаива- ния, см/сек	(3) Работа ад- гезии \times $\times 10^{-5}$, эрг/см ²	(4) Квазирав- новесная работа ад- гезии \times $\times 10^{-5}$, эрг/см ²
Сталь (5)	0,300	6,84	0,56
	0,100	4,68	0,60
	0,025	3,73	0,54
Латунь (6)	0,300	5,98	0,97
	0,100	5,10	0,98
	0,025	3,04	0,88

Key: (1). Base. (2). Velocity of stratification, cm/s. (3). Energy of adhesion $\times 10^{-5}$, erg/cm². (4). Quasi-equilibrium energy of adhesion $\times 10^{-5}$, erg/cm². (5). Steel. (6). Brass.

As can be seen from the dependence of value M_c from the thickness of film on basis of ODA-1200 (Fig. 155), the effective density of the cross-linking of free film, i.e., the film, obtained virtually in the absence of reaction polymer - solid surface, in an interval being investigated it does not depend on thickness. Value M_c of films on bases to a considerable degree is determined not only by the presence of rigid surface, but also by the nature by the latter. In films on steel and brass, the adhesion of polyurethane coatings to which is higher than to aluminum, difference in value M_c with free film is somewhat higher than for aluminum. This is obvious, it is bonded with the fact that in the case of brass and steel is formed a larger number of contacts of polymer chains with surface, which decreases M_c .

With an increase in the thickness of coatings, the difference between M_c free films and films on base decreases also with the thickness of 120 μ and above M_c in both cases they become identical.

These results confirm conclusions about the fact that the effect of rigid surface substantially is reflected in structure of both linear and cross-linked polymers it stretches at the significant depth of polymer depending on nature and physical state of the latter

[64]. Therefore by us for obtaining the comparable results during determination M_c of films on base are used films in thickness to 40 μ [54, 78]. Is investigated the dependence of the adhesion of polyurethane coatings on the nature of oligoester, and also its molecular weight and network density [78].

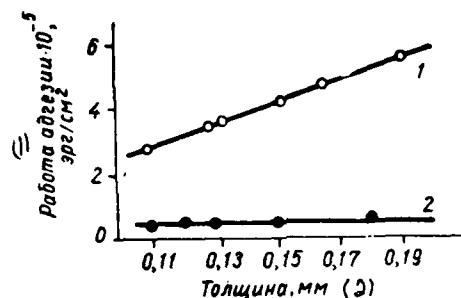


Fig. 154. The dependence of energy of adhesion on the thickness of the coating of base made of steel with NCO/OH=2:1:

1 - unstick speed 0.025 cm/s; 2 - quasi-equilibrium energy of adhesion.

Key: (1). Work of adhesion $\cdot 10^{-5}$, erg/cm². (2). Thickness, mm.

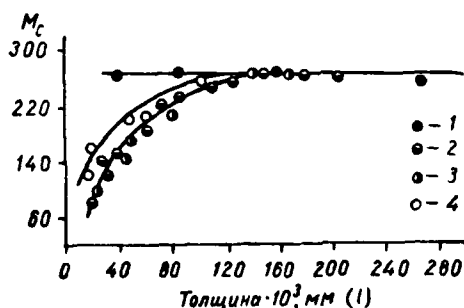


Fig. 155. Dependence M_c on thickness of film on basis of ODA-1200:

1 - free film; 2 - on steel; 3 - on brass; 4 - on dural;

Key: (1). Thickness • 10^3 , mm.

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As oligoesters are taken oligodimethyleneglycoladipate of molecular weights 600 and 120 (ODA-600 and ODA-1200) and TGF - 25o/o of OP-1200.

The dependence of value M_c from relationship/ratio NCO/OH, which characterizes the chemical density of cross-linking for coatings on basis of ODA-1200 (Fig. 156), shows that in all curves is observed the more or less expressed minimum in region NCO/OH=2:1. Obviously, initially with growth NCO/OH occurs an increase in the effective density of cross-linking, which was observed and it is earlier [73, 79]. With NCO/OH=4:1 effective network density falls as a result of certain decrease of a number of chemical and physical nodes. It is bonded with the formation of defective chemical grid due to the strong limitation of mobility of chain at deep stages of reaction. With NCO/OH=2:1 the effective density of cross-linking is greatest. This is reflected also in the value of the quasi-equilibrium energy of adhesion, determined for the present instance. As can be seen from Fig. 157, there is an extreme

dependence between the value of adhesion and the chemical density of cross-linking. With $NCC/CH=2:1$ (small M_c) occurs the greatest adhesion. But if we present the dependence of adhesion on the value of the common/general/total, effective density of cross-linking, which encompasses chemical and physical nodes, then is observed the symbatic dependence of energy of adhesion on M_c (see Fig. 157).

On the basis of Fig. 156 and 157, it is possible to draw a conclusion about the effect of the nature of base on the adhesion: polyurethane coatings on the basis of oligodiethyleneglycoladipate (mol. weight 1200) as coating on the basis of simple oligoesters [79], possess high adhesion to bases with the greater surface energy (steel, brass).

Is interesting to compare the results according to the adhesion of coatings on the basis of complex oligoester with the adhesion of coatings on the basis of simple oligoester of the same molecular weight. Table 71 depicts data according to quasi-equilibrium energy of adhesion it is polyurethane on basis of ODA-1200 and of copolymer to tetrahydrofurane oxide or propylene from which it is evident that the system of a change of the capacity of adhesion in dependence on the nature of base is identical. At the same time the adhesion in the case of simple oligoester is higher than for the same complex molecular weight. This can be, obviously, connected with difference

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in interaction energy of polymer chains with each other in both cases.

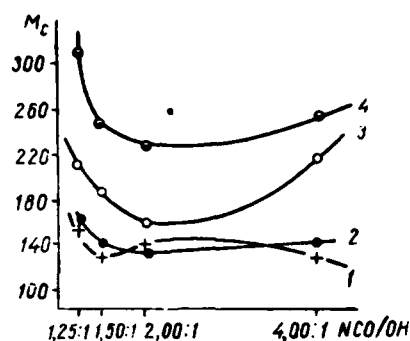


Fig. 156. The dependence of value M_c from the relationship/ratio of NCO/OH--group for coatings on basis of ODA-1200:

1 - steel; 2 - brass; 3 - dural; 4 - free film.

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It is known that intermolecular interaction in polyurethane on the basis of complex oligoester is considerably more than in simple ones [114]. It is logical therefore that the flexibility of the cuts of the chains between nodes for complex oligoesters is less and, therefore, their adaptability to surface worse than the cuts of chains it is polyurethane on the basis of simple oligoester. In connection with this a number of contacts polymer - the surface of coatings on the basis of complex oligoesters will be less than on the basis of simple ones, which leads to the decrease of adhesion first.

It is necessary to still bear in mind different reactivity of simple and complex oligoesters, that must be reflected in the structure of the grid of those formed it is polyurethane and during the adhesion of the latter to different surfaces.

For the investigation of the effect of molecular weight of initial complex oligoester on adhesion, are obtained the coatings on the basis of oligodiethyleneadipate of molecular weights 600 and 1200.

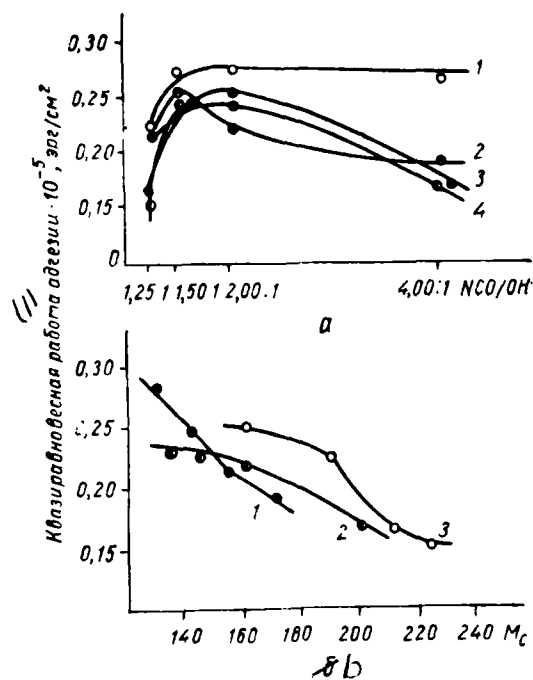


Fig. 157. The dependence of quasi-equilibrium energy of adhesion on relationship/ratio NCO/OH (a) and values M_c (b) for films on basis of ODA-1200:

1 - steel; 2 - brass; 3 - dural; 4 - glass.

Key: (1). Quasi-equilibrium energy of adhesion · 10⁻⁵, erg/cm².

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Table 72 depicts the value of the quasi-equilibrium energy of

adhesion of coatings on basis of ODA-600 and CDA-1200. Energy of adhesion for ODA-600 in all cases is more than for coatings on basis of ODA-1200. An increase of the concentration of polar groups per unit of volume because of the decrease of molecular weight of oligoester and an increase of the possibility of the formation of bonds polymer - surface is the reason for the observed differences.

Let us examine the bond between the determined experimentally by value M_c and adhesion of coatings on basis of ODA-600.

a change in experimental value M_c with growth NCO/OH for films on basis of ODA-600 in the presence of different bases (Fig. 158) shows that the effective density of the cross-linking of free film is more than films on the surface of brass and of dural, but it is somewhat less than on glass and steel. On the decrease of the effective density of films on the basis of complex oligoesters of light molecular weights in the presence of rigid surface in comparison with free film, has already been communicated [67].

Table 71. Dependence of the quasi-equilibrium energy of adhesion (10^{-5} erg/cm²) of polyurethane coatings on nature of oligoester, relationship/ratio NCO/CH and on type of rigid surface.

(1) Подложка	ОДА-1200				ПФ - 25% ОП-1200	
	1.25:1	1.5:1	2:1	4:1	2:1	4:1
Сталь (2)	0.23	0.28	0.28	0.28	0.47	1.97
Латунь (3)	0.22	0.26	0.23	0.20	0.34	1.50
Дюрал (4)	0.16	0.25	0.25	0.17	0.34	0.75
Стекло (5)	0.17	0.25	0.26	0.18	0.27	0.30

Key: (1). Base. (2). Steel. (3). Brass. (4). Dural. (5). Glass.

Table 72. Quasi-equilibrium energy of adhesion of polyurethane coatings on the basis of complex oligoester.

(2) Олигоэфир	NCO OH	[NCO] · 10 ⁴ , (3) моль/см ³	(1) Квазиравновесная работа адгезии · 10 ⁻⁵ , эрг/см ²			
			(4) Сталь	(5) Латунь	(6) Дюраль	(7) Стекло
ОДА-1200	1.25:1	1.17	0.23	0.22	0.16	0.17
	1.5:1	1.24	0.28	0.26	0.25	0.25
	2:1	1.50	0.28	0.23	0.25	0.26
	4:1	2.16	0.28	0.20	0.18	0.18
ОДА-600	1.25:1	1.85	0.64	—	0.32	0.68
	1.5:1	2.04	1.24	0.59	1.24	1.18
	2.0:1	2.22	1.45	1.24	1.27	1.33

Key: (1). Quasi-equilibrium energy of adhesion · 10⁻⁵, erg/cm². (2). Oligoester. (3). mole/cm³. (4). Steel. (5). Brass. (6). Dural. (7). Glass.

This anomaly they relate with the effect of rigid surface on the polymerizing processes, leading to the formation of more defective grid.

On the other hand, it is possible to assume that an increase in the hardness of polymer chains during the decrease of molecular weight of oligoester contributes to smaller number of their contacts with surface. The latter fact can be checked during the determination of adhesion. So, value M_c in films on brass and dural is almost identical and it is more than free film, as can be seen from Fig. 158. However, adhesion to dural they are investigated coatings considerably higher than to brass (Fig. 159). Consequently, with the formation of coatings on brass decreases a number of contacts polymer - surface, in the case of dural, the increase in the number of contacts of polymer chains with surface, which leads to an increase in the adhesion in comparison with brass, is simultaneously accompanied by the decrease of a number of nodes in volume, which is reflected in value M_c .

Concerning steel and glass, in these cases is observed the greatest adhesion of films on ODA-600 and the greatest effective network density (see Table 71, Fig. 161).

Thus, the decrease of molecular weight of initial oligoester

leads, on one hand, to an increase in the adhesion, on the other - is changed order in the series/number by the nature of bases, establish/installed earlier for oligoesters on basis of ODA-1200 and simple oligoester [73]. So, if adhesion was changed in series/number steel > brass > dural > glass and was located in accordance with the value of the surface energy of the materials being investigated, then in the case of coatings on basis of ODA-600 this series has the following form: steel > glass > dural > brass.

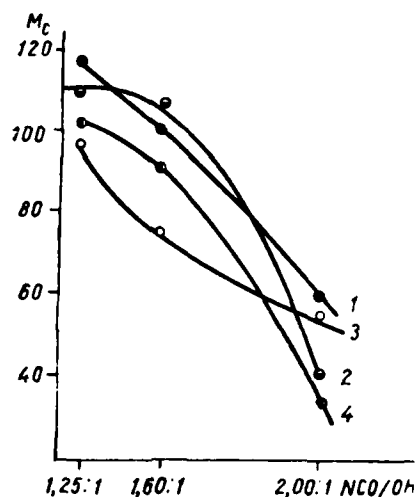


Fig. 158. The dependence of value M_c from the relationship/ratio of NCO/OH--group for coatings on basis of ODA-600:

1 - brass; 2 - dural; 3 - glass; 4 - free film.

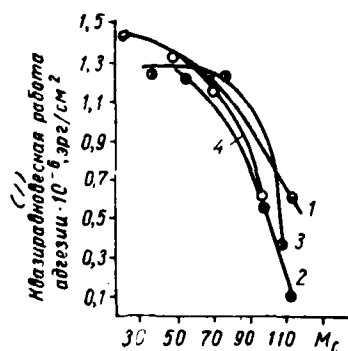


Fig. 159. Dependence of quasi-equilibrium energy of adhesion on value M_c for coatings on basis of ODA-600:

1 - steel; 2 - brass; 3 - dural; 4 - glass.

Key: (1). Quasi-equilibrium energy of adhesion $\cdot 10^{-6}$, erg/cm².

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The authors [54] assume that this inversion in series/number, just as the dependence of adhesion on the nature of the bases being investigated, to a considerable degree can be bonded with structurization, which occur on interface with rigid surface, determined by the nature of the latter and by structure initial component of polyurethane.

Thus, the analysis of scarce of works, dedicated to the study of adhesion is polyurethane, it speaks that the adhesive properties of the coatings being investigated are determined, in the first place, by their chemical structure, and namely by the nature of oligomeric units, isocyanate, crosslinking agent; the secondly, by the structure of grid, which is generated during the solidification of coatings on base. The application/use of units of different flexibility in chains it is polyurethane and the bases of different nature - all this changes the structure of grid, the relationship/ratio of physical and

chemical bonds in it and at the same time determines the adhesive properties of polyurethane coatings.

PROPERTIES AND STRUCTURE OF ELASTOMERIC POLYURETHANE FIBERS.

Recently there have been developed new materials on the basis of the linear polymers, developing under specific conditions properties of elastomers, but under the elevated temperatures or the influence of the solvents of those behaving as common thermoplastic materials. The discussion deals with the polymers which in the conditions/mode of exploitation develop elastic properties in the absence of the sufficiently strong/durable chemical bonds, which unite separate macromolecules into single three-dimensional/space grid.

Such a high elasticity is bonded with the flexibility of the chains of the macromolecules, which contain the groups which under conditions of operation are found as at the temperature of lower than the temperature of the vitrification of these sections of polymer chains. These systems will be called the common/general/total elastoplastics. A typical example of elastoplastics are the linear and weakly cross-linked polyurethane which serve as initial material for obtaining highly elastic polyurethane fibers. The schematic structure of such molecules is represented in Fig. 160. The soft segments, formed by linear networks, for example by the chains of

oligoesters, which form part of polyurethane molecule, are under the conditions for exploitation in highly elastic state. The temperature of the vitrification of the rigid segments of the sections of isocyanate component under normal conditions is considerably higher. Thus, rigid segments compose the nodes of physical three-dimensional/space grid, which as a whole is capable of the high reversible elastic deformations and it is not capable of flow at common temperatures.

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An increase in the temperature leads to the decomposition of physical nodes, and sometimes also weak chemical (for example, allophanate or biuret), and system acquires capability for viscous flow, which makes it possible to process this polymer by the common methods, used for thermoplasts.

The methods of obtaining and some properties of thermoplastic ones it is polyurethane with the labile chemical bonds, which disintegrate at high temperatures and are restored at low, they are presented in work [342].

The described principle of the construction of chain is the basis of the synthesis of the linear or weakly cross-linked

polyurethane elastomers from which by the methods of dry or wet molding are the fibers (of type spandex, Lycra, etc.), which possess high strength (0.6-0.8 g/denier), by high reversible elongation (500-800%) and by module/modulus, two or three times exceeding the modulus of elasticity of rubber fibers. The difference for such fibers from others synthetic ones, for example polyamides, is in the fact that the latter after extract acquire the oriented stable structure, which does not disappear after the release of tensile stress, while polyurethane fibers are capable of spontaneous reversible reset.

For a comparison are given the curves of the dependences of voltage/stress from deformation for the oriented polyamide, polyurethane elastic and rubber fibers (Fig. 161).

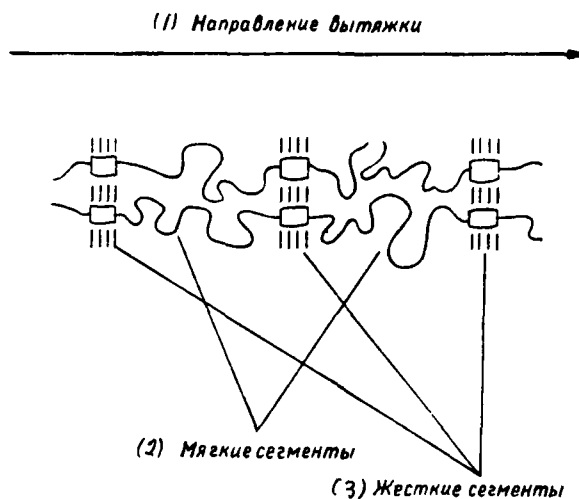


Fig. 160. Principle of the construction of the meristic urethane elastomer from rigid and soft segments.

Key: (1). Direction of stretching. (2). Soft segments. (3). Rigid segments.

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Elastic polyurethane fibers can be obtained on the basis of the three-dimensional/space cross-linked and thermoplastic polymers. They strongly differ in their elastic properties and are characterized by high strength and elongation.

Is shown the possibility of obtaining on the basis of linear ones it is polyurethane the fibers, which possess the properties, intermediate between highly elastic polyurethane draw plates and fibers of the type perlon. This is bonded with alternating in the polymer chain of the polyether/polyester and glycol units of different nature and entering the composition of polymer in different relationship/ratios [23, 24].

Fibers from elastic ones it is polyurethane it is possible to obtain, as already mentioned, on the basis of linear ones and those partially cross-linked, was polyurethane. The process of cross-linking in such systems, however, does not change the character of the solution, in which occur/flow/lasts the synthesis and which is used then for processing/treatment, i.e., in solution is not observed the gel formations, which impedes obtaining fiber. This fact of weak cross-linking, characteristic for obtaining highly elastic polyurethane fibers, is the additional confirmation of the fact that the role of the nodes of three-dimensional/space grid, which are determining elasticity and absence of flow, perform the physical nodes, formed by the reaction of rigid segments.

Difference to maturing degrees in spinning solutions it is possible to illustrate as follows [297]. Let us examine the dependence of ductility/toughness/viscosity on the concentration of

the solution of polyurethane in dimethyl formamide (Fig. 162) [297]. Curve 1 is characteristic for the polymer, obtained under soft conditions during the reaction of the mole of polyether/polyester (mol. weight 2000) and of mole of diphenylmethane diisocyanate.

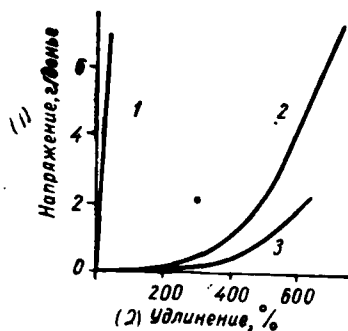


Fig. 161. Failure diagram is - elongation for different fibers:

1 - oriented poliamide; 2 - polyurethane; 3 - rubber.

Key: (1). Voltage/stress, g/denier. (2). Elongation.

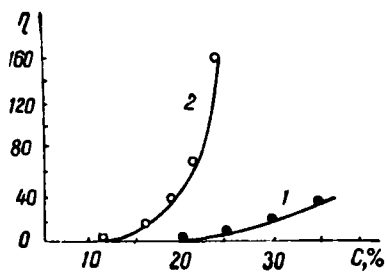


Fig. 162. Dependence of ductility/toughness/viscosity on concentration of solution of polymer in dimethyl formamide:

1 - on basis of polyethyleneglycoladipate (mol. weight 20000) and of

diphenylmethane diisocyanate; 2 - the same polyurethane, cross-linked with hydrazine bridges.

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Curve 2 characterizes the properties of the solution of macro-diisocyanate, obtained from the same initial products, but connected by hydrazine bridges. In this case the ductility/toughness/viscosity increases considerably faster with concentration, which is explained by the greater degree of branching and intermingling of the coiled molecules as a result of the cross-linking of chains with each other. The differences indicated are even more visual, if we compare the ductility/toughness/viscosity of the dilute polymer solutions in hexamethylphosphoramide after heating at different temperatures. The ductility/toughness/viscosities of 10/0 solutions are virtually identical, although initially there are noticeable differences. This is caused by the fact that in the case of the weakly cross-linked polymer during heating is feasible the break of weak bonds under the action/effect of solvent. The regulating of the maturing degree of fibers in spinning process by applying different crosslinking agents gives the possibility to change the properties of the obtained fibers.

Let us examine now some mechanical properties of elastic polyurethane fibers. Let us elongate, for example, highly elastic fiber to the specific value (to 2000/o) and after this let us dump. In this case, is observed hysteresis, shown in Fig. 163, for fibers of Lycra.

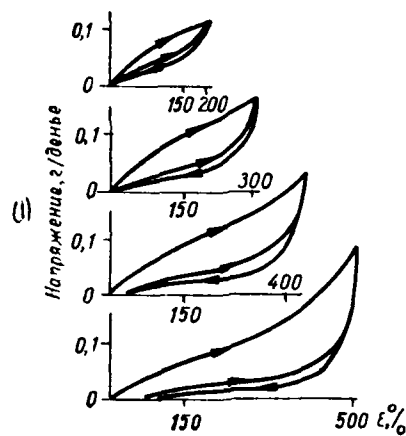


Fig. 163. Failure diagram is - elongation for fiber of Lycra.

Key: (1). Voltage/stress, g/denier.

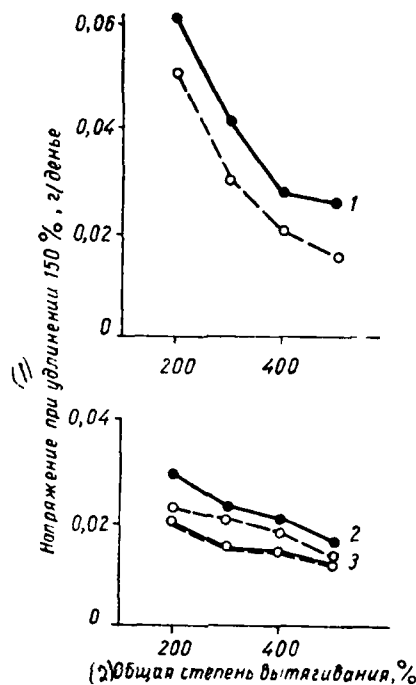


Fig. 164. Failure diagram - elongation for fibers of different degree of stretch with repeated drawing:

1 - Lycra; 2 - Viryne; 3 - rubber (unbroken curves with loading, broken - during removal of load).

Key: (1). Voltage/stress with elongation 150%, g/denier. (2). Common/general/total degree of stretch, %.

With repeated stretching the curve of the loading of the first cycle no longer is reproduced and lies/rests considerably below. This indicates that the structure, which arose with the formation of fiber, with the first drawing strongly is changed, as a result of which descends the voltage/stress, necessary for repeated drawing of the fiber. If according to diagram elongation - voltage/stress for fibers with different degree of stretch is compared the value of the voltage/stress, necessary for repeated drawing of the fiber to 1500% in dependence on the common/general/total degree of stretch (Fig. 164), then for different elastomers graphs substantially differ. With repeated stretchings hysteresis gradually disappears.

These phenomena resemble the known effect of Mullins [92] for the filled elastomers, and they also correspond to the effects, which have described we in the examination of the dependence of the properties of polyurethane elastomers on temperature and solvents. Differences in the elastic properties of polyurethane and rubber fibers are visible also from Fig. 165 [281], where they are shown to the dependence of voltage/stress from time during the different assigned elongation, to aging during this elongation during 30 s and to unloading. As is evident, in polyurethane fibers at the initial moments after unloading, more rapidly proceed the relaxation processes, especially during higher original elongation. Figure 166 gives dependence of the values of elongation from time with constant

load for polyurethane and rubber and some data on the amounts of residual deformations.

From data on temperature dependence of module/modulus and elastic after-effect after double stretching to 300c/o after 30 s after unloading (Fig. 167) it is evident that the elastic properties of rubber little vary with temperature, and for polyurethane such changes are very significant. Really/actually, if for rubber vitrification temperature lies/rests at region of $-50--70^{\circ}\text{C}$, then for the rigid units of polyurethane the region of vitrification is located considerably above. This explains more high tension, are necessary for the deformation of rubbers the smaller values of elastic after-effect. Moreover, until now, clearly are not establish/install the temperatures of the vitrification of the so-called rigid units.

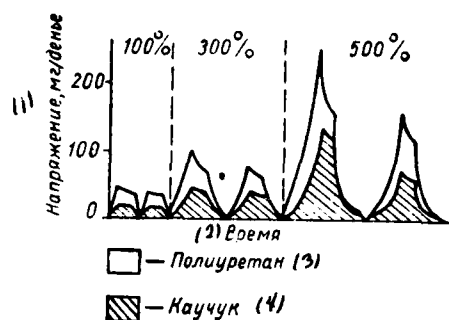


Fig. 165. Trajectory in the voltage/stress with different degree of stretch for polyurethane and rubber.

Key: (1). Voltage/stress, mg/denier. (2). Time. (3). Polyurethane. (4). Rubber.

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Therefore, the given reasonings bear thus far even qualitative character, although some quantitative dependences of change of the temperatures of the vitrification of elastic ones it is polyurethane with a change in the nature of unit, molecular weight and quantity of urethane groups they are given in Chapter IV.

The data on the dependence of the physical properties of polyurethane elastomeric fibers on their chemical nature it is small,

since, the majority of fibers is the property of firms and their chemical composition is not known to sufficient degree. However, it is interesting to bring some properties of fibers with an increase in the concentration of rigid segments (Fig. 168) [298]. As is evident, in this case, grow/increases the module/modulus and falls elongation, is increased also heat resistance (in this case the temperature, to which it is retained the stability of size/dimensions). The same factors determine the restorability of fiber after the removal of load.

The data of regularities are not specific in comparison with the effect of the same factors to the properties of polyurethane elastomers and therefore, further to stop on them is inexpedient. Hence, it follows that in elastomeric fibers is inherent the characteristic feature it is polyurethane: the structural grid, formed by mobile service, is capable of rearrangement under deformation or effect of temperature, which determines its mechanical properties.

In connection with the special feature/peculiarities of the mechanical behavior of elastic polyurethane fibers presented it is necessary to examine the scarce presentation/concepts of the structure of such fibers.

Is up to now carried out actually only one detailed analysis of the structure of fibers of the type of Dorlastan [173, 298]. The presentation/concepts of structure are based in the diagram of alternating in the chain of the rigid and soft segments, which generate the regulated and disordered regions (Fig. 169).

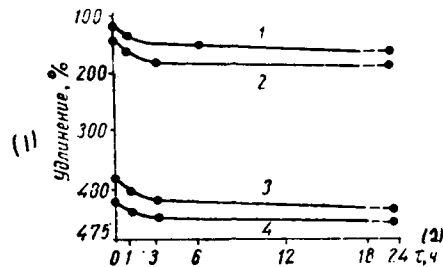


Fig. 166. the curves of the relaxation of the deformation of different elastomeric fibers.

1 - Lycra; 2 - spandex; 3 - Vilryne; 4 - rubber.

Key: (1). Elongation. (2). τ , h.

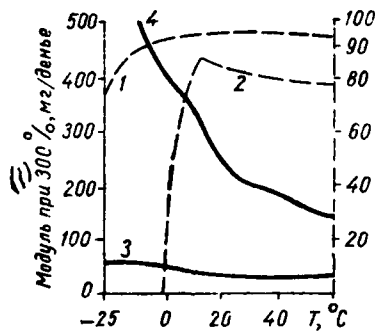


Fig. 167. Temperature dependence of module/modulus and permanent elongation of different elastomeric fibers:

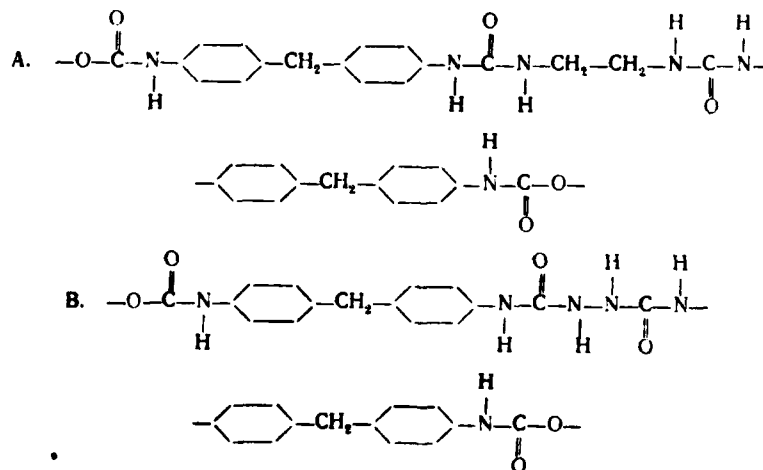
1 - elastic reduction after stretching to 300c/o for rubber; 2 - for Lycra; 3 - module/modulus of rubber; 4 - module/modulus of Lycra.

Key: (1). Module/modulus with 3000/o, mg/denier.

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This diagram completely corresponds to the very old diagram of the amorphous crystalline structure of polymers, conducted even by Alfrey [2] and based on model German - Gernogross. However, in old models it is assumed that the ordered and disordered regions were formed by the links of the same chemical nature.

Bonart investigates polyurethane with the rigid segments of the following types:



These rigid segments are cross-linked with soft units by

ethylenediamine or hydrazine. Some segments in that case are mixed polyesters (I) or polyethers (II). The author will remove/take X-ray photographs was polyurethane type A-I, B-I and E-II, since a polymer of the type A-II is badly/poorly soluble.

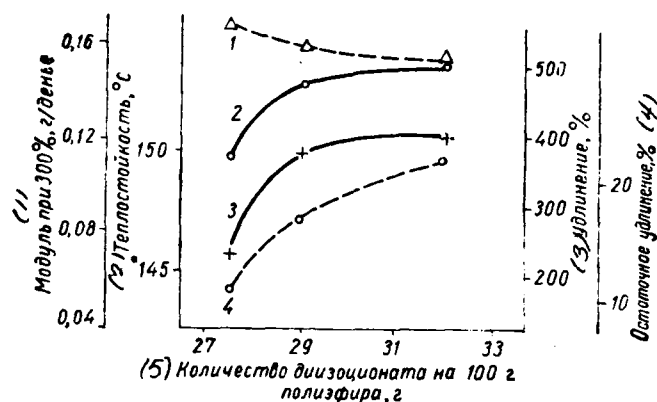


Fig. 168. The dependence of the mechanical properties of elastomeric fibers on the content of the rigid segments:

1 - elongation; 2 - module/modulus; 3 - heat resistance; 4 - permanent elongation.

Key: (1). Module/modulus with 3000/o, g/denier. (2). Heat resistance, °C. (3). Elongation. (4). Residual elongation. (5). Quantity of diisocyanate on 100 g of polyester, g.

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The X-ray photographs of the nonstretched and not to heat-treated specimen/samples show wide amorphous halo with two interferences.

During elongation 500o/o in polyurethane B-II, appears the X-ray photograph, characteristic for fiber as a result of crystallization with the stretching of the soft segments of chains. In rigid segments (Fig. 170) the arrangement of type 1 with four hydrogen bridges is energetically more preferable than arrangement 1" with two bridges. In real system can occur alternating different arrangements of chains relative to each other (for example, 2 and 2'). The same picture is possible for segments of the type B.

The complex picture of the three-dimensional/space arrangement of rigid and soft segments leads to the fact that during the extract of polymer the orientation of soft and rigid groups can be different. Bonart will show that during elongation to 200-300o/o rigid segments were oriented predominantly sloping to the direction of deformation, whereas soft - along the direction of orientation (Fig. 171a). Further stretching leads to the reorientation of the rigid units of chains (Fig. 171b).

It is interesting that during the heat treatment of oriented filament are observed relaxation, which lead to the almost full/total/complete disorientation of soft segments; the orientation of rigid segments is not disturbed.

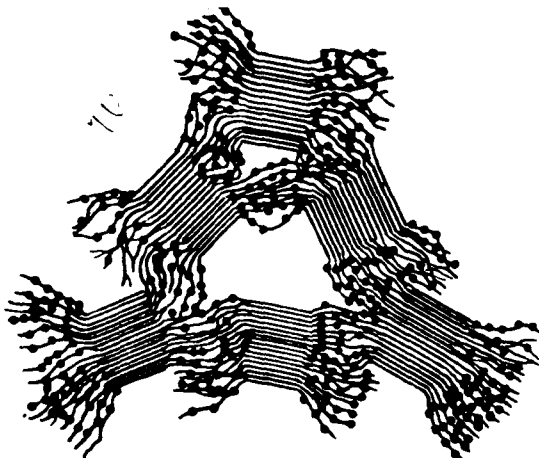


Fig. 169. Diagram of the structure of the ^{re-elongated} fiber.

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The thermal stabilization of fiber, obviously, is bonded with the decomposition of the part of cross connections in such a way that the rigid segments begin to be furnished along the direction of orientation. The decomposition of the part of the bonds during extract leads to the increase in the elongation resistance to which does not correspond to large restoring force, which is bonded with the known phenomena of softening under the action/effect of voltage/stress, analogous to hysteresis with load and unloading. In this case one must take into account not only hydrogen bonds, but

also possibility of the formation of nodes as a result of the reaction of the π -electrons of benzene rings. According to roentgenographic data, lattice parameters in this case $a=5$, $b=4$, $c=12.5\text{\AA}$, $\gamma=67^\circ$.

However, in the X-ray photographs of specimen/samples of the type A-I or B-I, is observed only paracrystalline arrangement of soft segments instead of the crystallization, caused by stretching. This picture corresponds to one equatorial reflex, which is joined with the statistical arrangement of links in the chain/network of undertaken polyether/polyester. The intensities of the observed reflexes can be changed during different processing/treatment of specimen/samples (during heating in water in the elongated state, etc.). X-ray picture is changed also upon transfer from polyurethane B-I to B-II. If for B-I reflexes are bonded with the specific orientation of soft segments, and with heat treatment this orientation disappears and appear the reflexes, caused by the ordering of rigid segments, then for B-II soft segments give only amorphous halo, and rigid segments are characterized by noticeable orientation. In order to obtain information about the regulated arrangement of one or the other forms of the segments of chain, Bonart will develop some principles of the theory of interference and will make the specific assumptions, concerning the arrangement of these segments in space during the orientation of polymer.

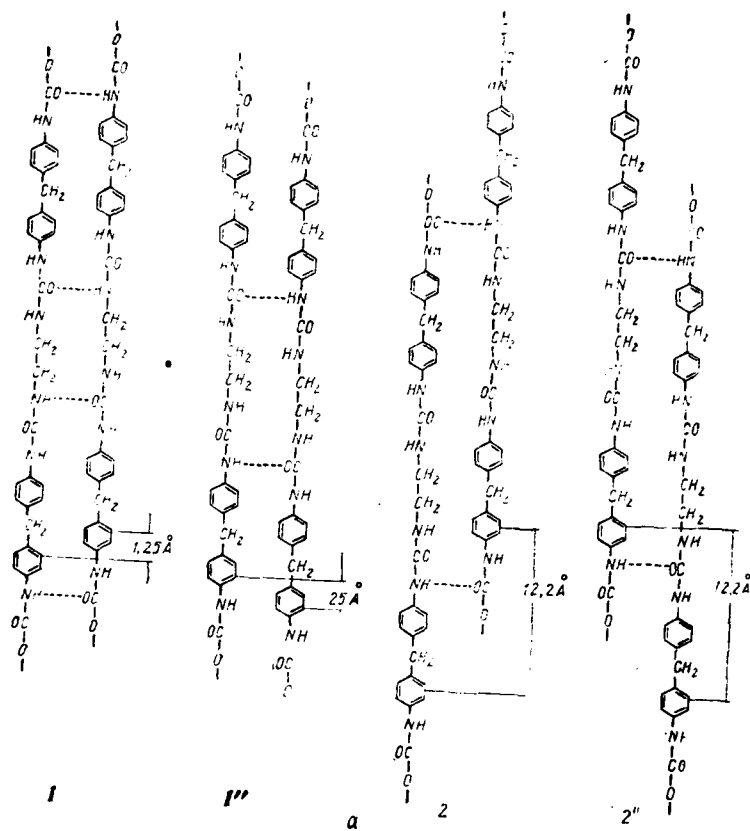


Fig. 170.

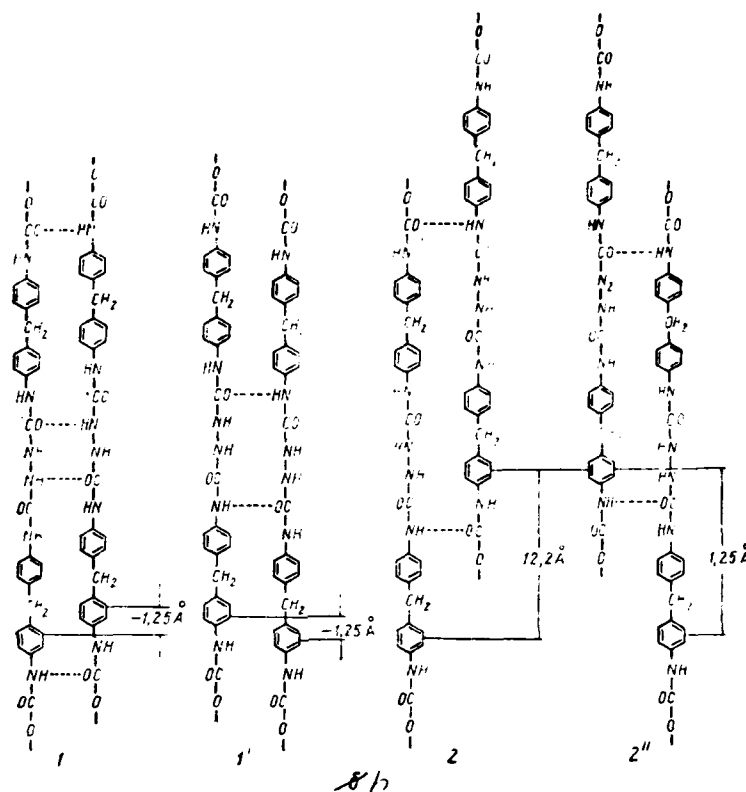


Fig. 170. Possible arrangement of the rigid segments A (a) and B (b), that leads to the formation of hydrogen bridges.

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Crystal structure of linear ones it is polyurethane as polyamides, it is substantially determined by the system of the hydrogen bonds whose arrangement in the case in question also must be

regulated in space. Figure 172 gives the possible diagrams of the layout of hydrogen bonds, based on Fig. 170, which can be compared with the results of roentgenographic investigation for segments of the type "A "and B. As can be seen from diagrams, most different possible arrangement of the hydrogen bonds between chains.

The X-ray analysis of the structure of elastomeric polyurethane fibers is given also in work [226]. The authors will examine the structure of the linear polyurethane elastomers, formed from rigid and soft units on the basis of simple and polyesters with molecular weights of 1000 and 4000.

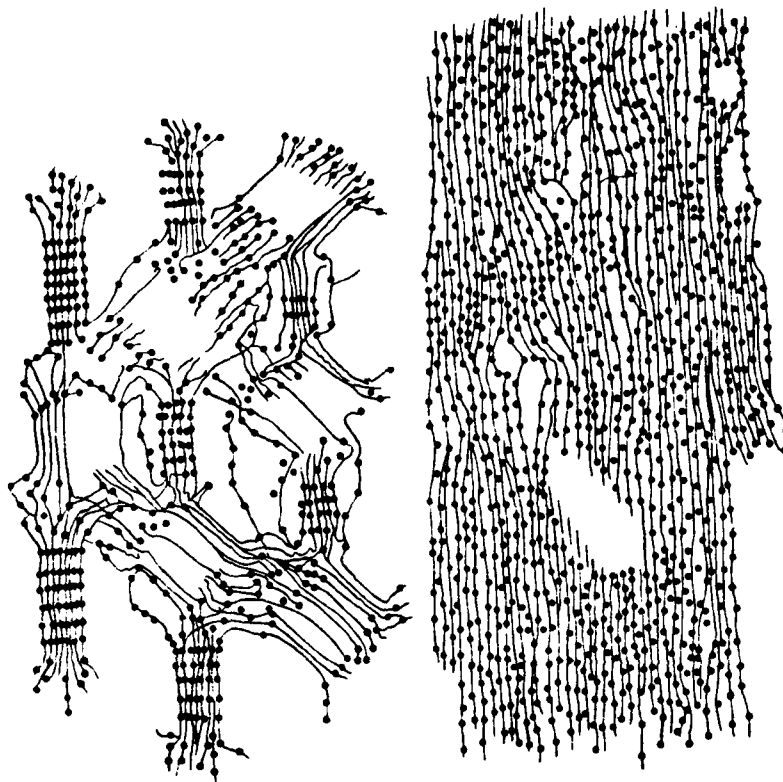


Fig. 171. Diagram of the fiber, elongated approximately to 200 (a) and 500 (b) o/o.

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In the disoriented state of the X-ray photograph of polymers, show diffusion halo and absence of structure. With stretching appear the discrete reflexes, which disappear during the removal of load. The authors assume that the reason for the high strength of fiber in

the elongated state is the crystallization with the stretching of the soft segments which compose 70-80% of entire polymer. Let us recall that Bonart observed on analogous elastomers during elongation to 200% virtually full/total/complete crystallization of soft segments and the systematic distribution of hydrogen bonds. The quantitative bond between the degrees of the crystallization of soft segments and drawing depends on the chemical nature of polymer.

However, the authors consider that the appearing with synthesis regular arrangement of soft and rigid segments in chain and appearing with the stretching of fiber picture make it possible to expect the specific ordering, also, in the re-elongated material. In this case, they assume that with the stretching of chain they slip relative to each other, while the strong dipole reactions between rigid segments do not begin to impede this sliding.

For the check of this hypothesis X-ray investigations at the small angles of elastomers on simple (Lycra) and on it is complicated (Dorlastan) polyether/polyesters. On the diagrams of the small-angle scattering of fibers with uninterrupted scattering for the re-elongated preparations, are visible crescent-shaped reflexes at equator, which correspond to periods 60 \AA for Dorlastan and $47-50 \text{ \AA}$ for Lycra. For Dorlastan there are two additional wide sickles on meridian, corresponding to distance 71 \AA . In spite of this the

authors are not inclined to consider initial materials as those regulated, ~~so~~^{since} after their three-hour extraction by methanol the reflexes indicated disappear. They, obviously, are bonded with the extracted substance. But the extracted preparations develop all the same discrete small-angle scattering. Such meridian reflexes can be bonded with the periodic oscillations of density in the direction of fibers whose average/mean periodicity comprises 95 Å for Dorlastan and 130 Å for Lycra. With stretching appear sharp reflexes. This gives to the authors the foundation for concluding that in polyurethane elastomeric fibers there are some types of structures, which depend on the composition of polymer and degree of its stretching.

In connection with the problem of elastomeric fibers, again arises a question concerning hydrogen bonds in the polyurethane elastomers which in large measure determine the structure of fiber. However, it should be noted that, for example, Rink [298] together with hydrogen bonds is added specific value to the common van der Waals reactions between the soft segments which, in his opinion, determine the effects of repeated deformation. It considers that for the overcoming of these bonds, which do not disintegrate completely during deformation, is spent the additional effort/force as a result of the preservation/retention/maintaining of certain degree of cross-linking according to the physical bonds which after the removal of load prevent the reduction of initial size/dimensions.

Pages 260-261.

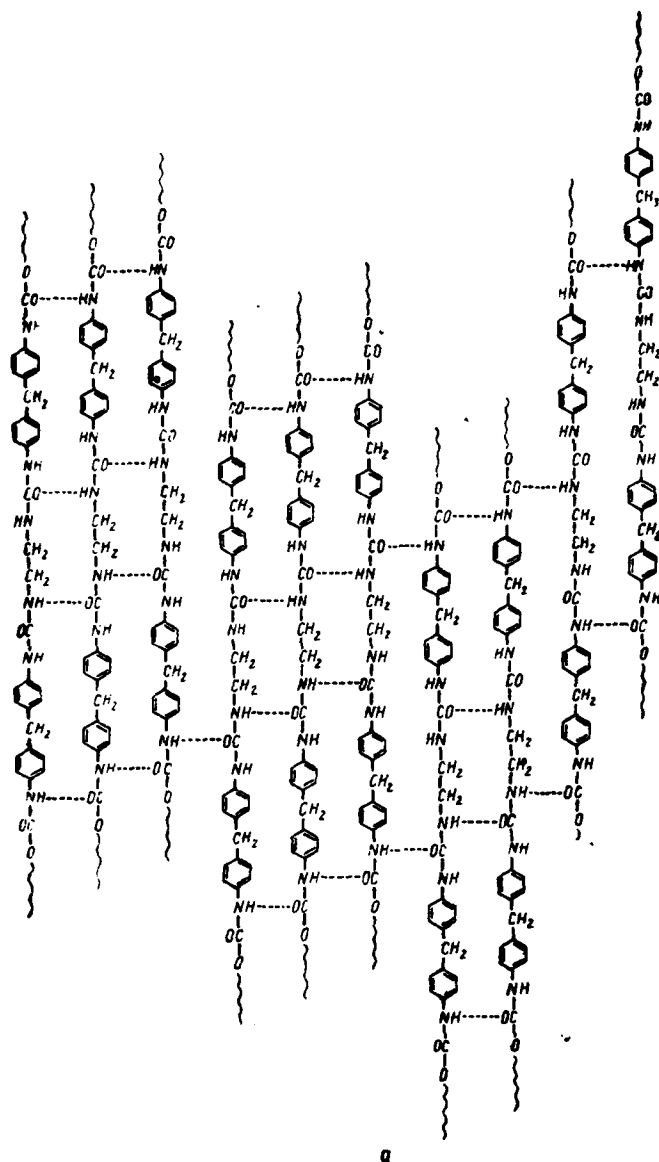


Fig. 172

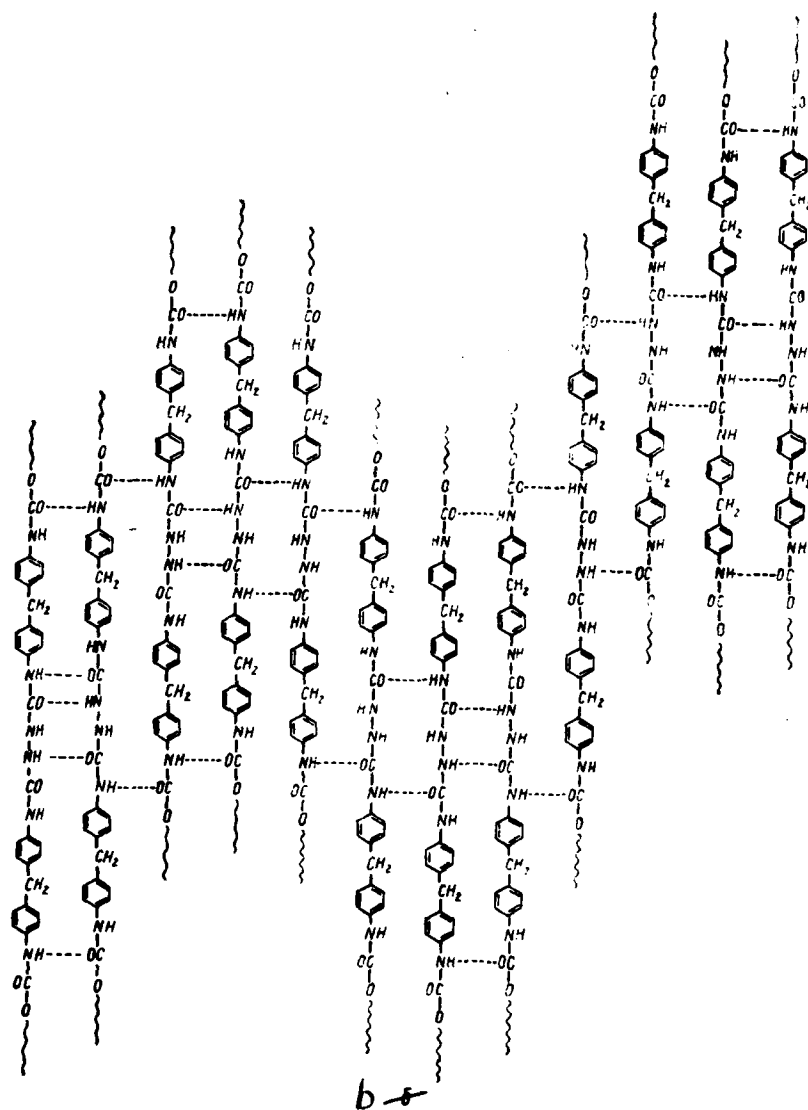


Fig. 172. Structure of cross connections between rigid segments A (a) and B (b).

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Presentation/concepts Rink will agree well with our about the thixotropic structural grid which determines basic properties it is polyurethane, and with the results of the rheological investigations, which indicate the important role of common physical reactions in the elastic properties of oligomers it is polyurethane. Really/actually, Rink it considers that with an increase in the temperature the strength of hydrogen bonds falls, moreover for rigid segments this is developed especially strongly at 130-190°C, in consequence of which physical bonds disintegrate, but they retain capability for reduction during a temperature decrease. We already note that this is - typical special feature/peculiarity of elastoplastics, which determines the possibility of the formation of rivers and thermal stabilization of the structures, appearing with moulding.

We will reveal/detect also the effects, bonded with the decomposition of bonds in region of 40°C, substantially affecting the properties of elastomers. Specific properties it is polyurethane (for example, high resistance to abrasion), that are inherent in both the rubbers and thermoplastic fibers of the type perlon, characteristic for elastic fibers. In the opinion Rink, high resistance to abrasion and decomposition under the effect of the voltage/stresses of polyurethane fibers in comparison with common ones is the result of

further cross-linking as a result of the formation of hydrogen bridges in rigid segments. Under the effect of mechanical stresses the partial possible decomposition and the reduction of the bonds between rigid segments, which is impossible for the chemical bonds which after decomposition no longer are reduced.

Consequently, the formation of the physical structural grid whose irregularity as a result of the structure of chain and structure of rigid segment is considerably more than in common rubbers, determines the basic physical properties of polyurethane elastomeric fibers.

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CONCLUSION.

The problem which place to themselves the authors in this monograph, is the establishment of the physicochemical special feature/peculiarities of behavior was polyurethane and the explanation of the reasons, differing this class of polymers from others. The study of this question is important, first of all, because polyurethane are the only class of the polymeric compounds on basis of which it is possible to obtain virtually all valuable types of polymeric materials - rubbers and plastics, common and elastomeric fibers, glues and coatings, sealing compounds and foamed plastics, etc.

The analysis of structure is polyurethane, the explanation of basic laws governing their formation, the study of the mechanical and physicochemical properties of linear ones and three-dimensional it is polyurethane and the properties of insulated circuits they make it possible to now establish/install the reasons on which the polyurethane occupy special position among other polymers. It is

determined by two basic factors: diversity of the chemical structure of polyurethane chains and by specific structure of the polymer chain, which is determining the structure of polymers in unit.

Distinctive features of chemical structure it is polyurethane they are determined by application/use for their synthesis of diisocyanates which are unique in the diversity of the chemical reactions in which they can accept collaboration. The use of diisocyanates of different chemical nature (aliphatic, aromatic, cyclic, etc.) considerably expands the possibilities of the variation of the chemical structure of those synthesized it is polyurethane. Application/use as the second component of the polyfunctional compounds of the most varied classes - from low-molecular glycols to oligomers and copolymers with hydroxyl end groups - leads to this diversity of the final chemical structure of polymers, whatever is observed in one of other classes of polymers. Entry in the chain of polyurethane many types of functional groups and structural units it makes it possible to widely vary the properties of polyurethane materials.

The additional possibilities of changing the properties it is polyurethane they are bonded with application/use for their cross-linking of different in their chemical nature compounds, capable of interacting with the isocyanate or hydroxyl groups. As a

result this content in the end product of the reaction of urethane groups it can be very insignificant. From this point of view, polyurethane generally cannot be considered the single class of polymers (as, for example, polyamides or polyacrylate), since only common/general/total sign is the presence in the chains of urethane grouping.

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Another special feature/peculiarity of chemical structure it is polyurethane it consists in the fact that for their synthesis are used the oligomeric units, which are actually the low molecular polymers and independently possess the combination of the physicochemical properties, to the inherent polymers. Application/use of oligomeric units of different chemical nature and, therefore, different flexibility of polymer chain gives grounds to consider polyurethane as the block copolymers in chains of which are alternated pliable and rigid units. Alternating the units of different chemical nature makes it possible to widely change properties it is polyurethane, that also determines the possibility of obtaining of them an entire gamma of polymeric materials. Meanwhile the principle of alternating units, specific for is polyurethane, still little used in practice. Is insufficiently carried out investigations in the development of the methods of the

synthesis of poly-block ones it is polyurethane, in which together with alternating of oligomeric and diisocyanate unit on chain is realized/accomplished another alternating of units themselves - simple, ester, copolymer, etc.

By certain demonstration of the principle of alternating units for the modification of properties it is polyurethane it is the introduction to polyurethane of units on the basis of oligodiene with the terminal hydroxyl groups, which leads to obtaining of elastomers. Obtaining oligourethaneacrylate with terminal double bonds will lead to the appearance of a new class of polymers - polyurethaneacrylate, matching properties was polyurethane and polymerizing plastics.

Thus, the special feature/peculiarities of chemical structure and the possibility of imparting to polyurethane different properties are determined, first of all, by the wide circle of the initial compounds, used for synthesis it is polyurethane and relating to different classes. It is possible to say that there is no problems it is polyurethane as such, exists the problem of initial compounds for the synthesis of the polymers, which contain urethane groups. Really/actually, in view of the diversity of the chemical structure of the molecular units, which belong to different classes (polybutadienes, polyether/polyesters, etc.), the polyurethane, obviously, cannot be considered as single class, on they must be

considered more widely as the group of the polymers of different classes, for which common/general/total is the presence in the chains of rare urethane groups - NCOO -. Even collaboration in the synthesis of diisocyanates - not necessary conditions for obtaining it is polyurethane, since are possible nonisocyanate methods of synthesis.

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In the examination of the special feature/peculiarities of physical and molecular structures, it is polyurethane, first of all, necessary to focus attention on the flexibility of polymer chains and intermolecular interaction between them. The nature of glycol and isocyanate units determines flexibility of the individual sections of chains and intermolecular interactions between them. This leads to manifestation with polyurethane of the properties of elastoplasts or thermoplasts. In the case of polyurethane elastomers, a change in molecular weight of polyether/polyester unit serves as one of the basic ways of the regulating of the properties of three-dimensional grid. The capability of unit for crystallization, which depends on molecular weight and chemical nature, in the final analysis determines the phase state of polymers and the level of their intermolecular organization.

... diversity of the heterobond in chain of polyurethane it

substantially affects their flexibility. The examination of data according to internal rotation in organic molecules shows, in particular, that the internal rotation around C-O-bond is facilitated in comparison with rotation around bond C-C. Therefore it is possible to assume that the polymer chains with heterobond of the *type of* polyethers possess increased flexibility.

On the other hand, the presence of the strongly interacting groups in chain must cause an increase in the barriers of internal rotation and becoming rigid of chain. The combination in one molecule of different types of bonds, most typical for it is polyurethane, is determined the complex character or the dependence of the flexibility of chains it is polyurethane on their chemical nature.

Great effect on the capacity of molecules it is polyurethane to a change in the conformations is had its own flexibility of oligomeric units whose contribution to the flexibility of chain is predominating. This very is substantial from that point of view, that the manifestation of the flexibility of molecules in polyurethane grids is not the exceptional result of the cross-linking into long of the sequence of short oligomeric chains, but the result of its own flexibility of oligomers. Its own flexibility of oligomeric units and possibility of strong intermolecular interactions between units is represented by essential feature it is polyurethane.

In three-dimensional/space grid it is polyurethane they are possible together with the chemical and hydrogen bonds between urethane and other groups the common Van der Waals reactions between the cuts of chains in riding-crop. The presence in the grid of such reactions whose degree depends on the chemical network density, changes the barrier of rotation and, thus, the flexibility of the cuts of the chains between nodes even when the distance between nodes exceeds the value of thermodynamic segment found for the not bonded in grid high-molecular chains.

A question concerning the role of intermolecular interactions in polyurethane very important, but specific character is polyurethane in this respect it is developed is only in the examination of three-dimensional cross-linked ones polyurethane.

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The diversity of functional groups in chain creates great possibilities for the formation of the molecular bonds of different nature and energy from hydrogen ones to Van der Waals ones. The significant role of such intermolecular interactions in the three-dimensional grid especially characteristic of polyurethane

elastomers. It is obvious, such reactions are not eliminated also for other rubberlike materials. It should be noted that if to the problem of intermolecular interactions in the linear polymers was given always much attention, then these questions were insufficiently lit in connection with three-dimensional polymers. The examination of the defects of grid and formation of wrapping and engagements of chains to a certain degree consider these reactions; however, not from the point of view of the formation of molecular bonds. Polyurethane are the system in which the role of intermolecular interactions in grid project/emerges especially distinctly.

One of the basic special feature/peculiarities of the structure of the grid of three-dimensional ones it is polyurethane it consists in the fact that in it the main role belongs not to the chemical, but physical nodes, formed as a result of intermolecular interaction with the collaboration of different functional groups of molecules.

The effective density of cross-linking in polyurethane is determined mainly by the secondary physical bonds, which are generated in three-dimensional grid as a result of the reaction of chains with each other. The large role of physical reactions is confirmed by the determinations of the energy density of the cohesion of polyurethane rubbers whose values are higher than for common rubbers.

The strong molecular bonds, which generate in polyurethane uninterrupted three-dimensional/space grid, in the specific cases lead to the fact that the linear polyurethane, "cross-linked" only with physical bonds, develop the properties, usually characteristic only for the chemical cross-linked linear networks.

Another special feature/peculiarity of the structure of three-dimensional/space grid in polyurethane it consists in its high mobility, i.e. capability for rearrangement under the influence of temperature or the mechanical effect. This conclusion follows from the anomalous temperature dependence of the elasticity modulus of such grids and from data of thermodynamics highly elastic deformations. The decomposition of molecular bonds in grid during heating or deformations leads to an increase in the distances between network points. The capability of grid for decomposition and rearrangement under the effect of temperature, solvents and mechanical loads gives grounds to examine a similar grid by analogy with the thixotropic structures, well studied in colloid chemistry. This presentation/concept will agree well with the results of the investigation of the flow properties of oligomers and macro-diisocyanates which confirm the high degree of thixotropy already in oligomeric systems.

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The presence of mobile structural grid in polyurethane conditions many specific properties. It is obvious, by the comparative lightness/ease of decomposition and subsequent reduction of grid it is possible to explain capability of polyurethane for self-healing of defects during deformations. Really/actually, with deformation, which especially intensively is developed in the places of stress concentration, occurs the noticeable decomposition of grid, as a result of which occurs seemingly thixotropic transition of polymer of the highly elastic to viscous flow state. Possible under conditions of act/effecting the deformation flow leads to the curing of defects in the most strained places. In this case, the load is distributed again more evenly and again are reduced the destroyed bonds.

The mobility of grid contributes, obviously, and to comparatively rapid equilibrium establishment and new structure, which corresponds to state of strain. This will occur, if the rates of deformation and rearrangement of structure are compared. Then in system during deformation is establish/installed the new equilibrium as a result of which at each stage of deformation will have to spend

work not only on the stretching of chains, but also on the decomposition of network points. This differs polyurethane from other elastomers where the decomposition is bonded predominantly with the deformation of chains.

The account the special feature/peculiarities of the physicochemical behavior is polyurethane it makes it possible to fit/approach the explanation of the reasons, which lead to the increased strength and resistance to abrasion. We assume that here the way to resolution of problem lie/rests through the study of mechanical and other properties of surface layers is polyurethane. It was recently establish/installed [22], that wear with friction are accompanied by the noticeable rearrangements of the structure of the surface layer of polymer. Under certain conditions this rearrangement leads to the structure, more resistant to abrasion. Molecular mobility in surface layers and structure of the surface layers of polymers differ from the same in volume [64, 76], which is bonded with the isotropy of the distribution of molecular bonds in volume and its absence in surface layer. These facts together with the consideration of the special role of physical reactions in polyurethane grids make it possible to present abrasion it is polyurethane as the specific relaxation processes in surface layers, bonded with thixotropic decomposition and reduction of the structure of surface layer.

The examined in this monograph laws governing the change of the properties it is polyurethane with structure variation and explanation of the series/number of the reasons for their specific behavior they give the possibility to disseminate the principles of the construction of polyurethane chains to other materials, and the realization in them of the series/number of the characteristics, which are inherent in polyurethane, will make it possible to fit/approach the creation of the wide circle of polymers and polymeric materials of different chemical nature which will possess the most valuable properties, which are inherent in polyurethane, and will be deprived of their deficiencies.

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